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CERTAIN ASPECTS OF THE CHEMOTHERAPY OF SYNTHETIC HYPNOTICS.*

By Sir Upendra Nath Brahmachari, Kt., M.A. M.D., Ph.D., F.R.A.S.B., F.N.I.

It is a great privilege to be asked to preside at the annual meeting of a learned society like yours, whose chair was previously occupied by distinguished persons like Sir P. C. Rây, Dr. Gilbert J. Fowler and other illustrious men. I have chosen for my discourse a subject which constitutes one of the most important applications of chemistry to medicine and therefore should interest the votaries of chemistry as well as of medicine.

As I stated in my presidential address at the Indian Science Congress last year (*Proc. Indian Science Congress*, 1936, p. 23) the demand for a suitable hypnotic has been intense in recent times, because due to the stress and strain of modern life, many ask for an ideal draught or a tablet or a pill that would gently put them in possession of 'tired nature's sweet restorer, balmy sleep.' From the hypnotics of olden times to recent ones, the chemist has travelled a long way, and he is still moving farther and farther in the search for better hypnotics.

The chief advances in our knowledge of hypnotic drugs in recent times have been (1) the discovery of many new derivatives of the barbituric acid series; (2) the introduction of a number of drugs other than alkaloids for purposes of basal anæsthesia. The barbituric acid derivatives are perhaps the most commonly used hypnotics at the present day. Other recent hypnotics not derived from barbituric acid include avertin, although alcohols, chlorinated alcohols, aldehydes and urithanes have also come to the forefront.

An ideal hypnotic should be free from any toxic effects, should be quickly excreted, give a quiet natural sleep of normal duration in a short time, should give rise to no addiction and leave no effects when one taking it wakes up in the morning. Such a hypnotic has yet to come. Further, the same hypnotic is not suitable for all types of cases and sometimes methods other than hypnotics are suitable for individual persons for relief of sleeplessness.

To Hyderabad the history of hypnotics must have a peculiar interest because the first Chloroform Commission in the whole of the world was held in this great city under the auspices of its illustrious Ruler. Here, as many of you may know, Lauder Brunton made his classical observations on anæsthetics, assisted by Lawrie and others. It was in India again that Waldie, who was one of the pioneers of chemical research in India and who lived in Calcutta, was associated with the discovery of the anæsthetic properties of chloroform in 1847. To his memory there is a tablet in the rooms of the Royal Asiatic Society of Bengal, containing the following words:

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* Presidential address at the thirteenth Annual General Meeting of the Indian Chemical Society at Hyderabad, Deccan, 1936.

In memory of

DAVID WALDIE

Born in Linlithgow, Scotland, February 27th, 1813, David Waldie was associated with the discovery in 1847 of the anæsthetic properties of chloroform. Arriving in Calcutta in 1853, he became the pioneer of chemical manufacture in India. He was an active member of this Society for twentyfive years and served on the Council for ten years. Died in Calcutta, June 23rd 1889.

As pointed out by Willcox, the classification of hypnotic drugs on a purely chemical or pharmacological basis is difficult and unsatisfactory. Hypnotic drugs of low toxicity are alcohols, bromides, etc. A chemical classification of the synthetic hypnotics may be more or less as follows: (1) the alcohols and aldehydes with or without a halogen radical, (2) the urea group, (3) sulphone or sulphone-alkyl group, (4) the barbituric acid group.

Alcohols and aldehydes with or without Halogens.

Chloral.
Chloralamide.
Chlorobutol.
Hypnal, a compound of chloral and antipyrine.
Dormiol, a compound of chloral and amylene hydrate.
Ural, a compound of chloral and urethane.
Isopral is trichloro*iso*propyl alcohol.
Bromal.
Paraldehyde.
Amylene hydrate.
Aponal, a compound of amylene hydrate and urea.
Hedonol is isomeric with aponal.
Neuronal, diethylbromide acetamide.
Avertin is tribromoethyl alcohol.

The Urea Group.

Urethane—Ethyl carbamate.

Aleudrin—Dichloro*iso*propyl carbamate.

Uradal or *adalin* is bromodiethyl acetylurea.

Uvaleral or *bromural* or *dormigene* is a monobromo*iso*valeryl urea.

Somnosal is a proprietary preparation composed of a mixture of bromural and dimethylaminophenylmethyl*iso*pyrazolon.

Voluntal—urethane of trichloroethyl alcohol.

Sulphone or Sulphone-alkyl Group.

Sulphonal is dimethylmethane diethylsulphone.

Trional is methylsulphonal.

Tetronal is ethylsulphonal.

The Barbituric Acid Group.

Barbitone or *veronal* is diethylbarbituric acid.

Sodium barbitone or *medinal* is the sodium salt of barbitone.

Proponyl is dipropylbarbituric acid, and

Neonal or *soneryl* is *N*-butylethylbarbituric acid.

Dial is diallylbarbituric acid.

Phenobarbitone or *luminal* is diphenylbarbituric acid.

Sodium luminal is its sodium salt.

Phanodorm is *cyclo*hexenylethylbarbituric acid.

Evipan is *N*-methyl*cyclo*hexenylmethyl barbituric acid, and

Sodium evipan or *evipal* is its sodium salt.

Pento-barbitone is ethylmethylbutylbarbituric acid, and its sodium salt is *Nembutal.*

Iprai is calcium ethyl*iso*propylbarbituric acid.

'*Allonal* is a combination of allyl*iso*propyl barbituric acid with amidopyrine.

Veramon, a combination of veronal with amidopyrine.

Gardenal is phenylethylbarbituric acid.

Cibalgin is a combination of dial and amidopyrine.

Somnifaine is a combination of allyl*iso*propylbarbituric acid and veronal.

Sodium hebaral is the sodium salt of hexylethylbarbituric acid.

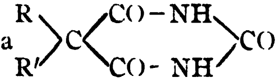
Beatol is a proprietary preparation said to be a mixture of veronal with extracts of valerian and jusquimane.

Quadronox is a proprietary preparation said to contain 80% veronal, with phenacetin, phenazone, etc.

Amytal is *iso*amylethylbarbituric acid.

Pernocton is 2-butylbromoethylbarbituric acid.

Sandoptal is *iso*butylallylbarbituric acid.

The barbiturates conform to the general formula  $\begin{matrix}R\\R'\end{matrix}>C<\begin{matrix}CO-NH\\CO-NH\end{matrix}>CO$ where R and R′ represent alkyl or aryl groups.

As already mentioned the barbituric acid derivatives are perhaps the most commonly used hypnotics at the present day. When taken by the mouth they are quickly absorbed and within an hour or so after a clinical dose sleep usually ensues.

The addition of alkyl or aryl radicles of higher molecular weight than ethyl adds to the toxicity of the substance, thus luminal, dial, proponal, gardenal, sonery1 and nembutal are all more toxic than veronal.

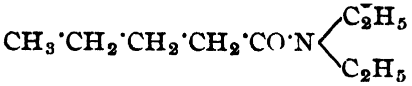
The combination of a barbituric acid compound with an analgesic drug such as amidopyrine, phenacetin, etc. occurs in veramon, allonal, cibalgin, and quadronox and appears according to some to be dangerous since the barbituric acid compound is much more toxic than the analgesic drug, and this may lead to an overdosage of the barbiturate when the preparation is taken in large doses to relieve pain.

Introduction of sodium in the barbituric acid group makes the product soluble. This confers greater speed in action—for example, barbitone sodium or medinal is far more soluble and quicker in action than simple barbitone or veronal. Solubility also makes it possible for one to inject the drug.

The simpler amides are without any appreciable narcotic action, and it it is only with the fifth and subsequent members of the series—valerylamide, $C_4H_9 \cdot CO \cdot NH_2$ that any signs of narcotic activity are shown. Aliphatic amides containing longer carbon chains than valerylamide and the next two members of the series show but little narcotic action, so that the range of simpler aliphatic amides showing such activity is confined to those containing the carbon chains, five, six or seven units in length.

The effect of replacing the hydrogen of the CH_3 group of acetamide by alkyl groups is said to increase its narcotic action.

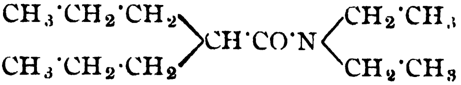
If valerylamide is converted to its *N*-diethyl derivative (I) it does not lose its narcotic activity. This has led to its use in dealing with hysterical or neurasthenic cases.



$CH_3\cdot CH_2\cdot CH_2\cdot CH_2\cdot CO\cdot N<\begin{matrix}C_2H_5\\C_2H_5\end{matrix}$

(I)

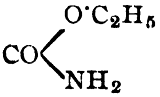
The complete replacement of ethyl groups of the *N*-hydrogen atoms in many of the acid amides, as in dipropylacetodiethylamide (II) leads to the formation of compounds without either narcotic or paralytic activity.



$\begin{matrix}CH_3\cdot CH_2\cdot CH_2\\CH_3\cdot CH_2\cdot CH_2\end{matrix}>CH\cdot CO\cdot N<\begin{matrix}CH_2\cdot CH_3\\CH_2\cdot CH_3\end{matrix}$

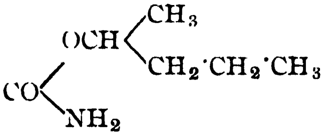
(II)

The urethanes occupy a place midway between the simple amides and ureas, and are the esters of the half amide of carbonic acid. They exert a pronounced narcotic action. Ethylurethane (III) possesses a mild narcotic action. Many of the substituted urethanes are more active than the parent



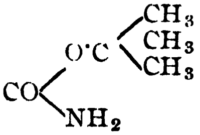
$CO<\begin{matrix}O\cdot C_2H_5\\NH_2\end{matrix}$

(III)



$CO<\begin{matrix}OCH<\begin{matrix}CH_3\\CH_2\cdot CH_2\cdot CH_3\end{matrix}\\NH_2\end{matrix}$

(IV)



$CO<\begin{matrix}O\cdot C\begin{matrix}CH_3\\CH_3\\CH_3\end{matrix}\\NH_2\end{matrix}$

(V)

ethyl derivative. Thus methylpropylcarbinol urethane (Hedonal, IV) has been advocated as a safe hypnotic for general use. The minimum narcotic dose values show it to be appreciably less narcotic than the simple ethyl urethane, but the tertiary butyl derivative (V) is more active. The introduction of halogen atoms, as is general with this type of compound, is attended with a considerable increase in narcotic activity. Thus αα′-dichloro*iso*propyl carbamic ester (Aleudrin, VI) has a minimum narcotic dose value When the NH_2-group is substituted by aryl residues as in phenylethylurethane (VII), the narcotic action disappears and an antiseptic action results. Whist the isomeric unsymmetrical dichloro*iso*propyl carbamic ester is claimed to be a useful hypnotic (Sen, *J. Indian Chem. Soc.*, 1924, **1**, 18; *Biochem. Z.*, 1924, **151**, 52), voluntal (Linter and Luers, *Z. physikal. Chem.*, **88**, 122; Willstäter, *Ber.*, 1923, **56**, 2283) is also used as a hypnotic, supply thereby a mitigated chloral.

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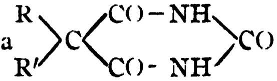
The barbiturates conform to the general formula  $\begin{matrix}R\\R'\end{matrix}>C<\begin{matrix}CO-NH\\CO-NH\end{matrix}>CO$ where R and R′ represent alkyl or aryl groups.

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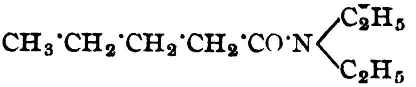

$$\mathrm{CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CO{\cdot}N}\left\langle\begin{matrix}\mathrm{C_2H_5}\\\mathrm{C_2H_5}\end{matrix}\right.$$

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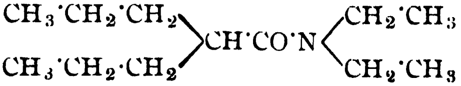

$$\left.\begin{matrix}\mathrm{CH_3{\cdot}CH_2{\cdot}CH_2}\\\mathrm{CH_3{\cdot}CH_2{\cdot}CH_2}\end{matrix}\right\rangle\mathrm{CH{\cdot}CO{\cdot}N}\left\langle\begin{matrix}\mathrm{CH_2{\cdot}CH_3}\\\mathrm{CH_2{\cdot}CH_3}\end{matrix}\right.$$

(II)

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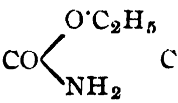
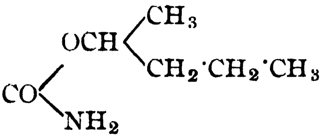


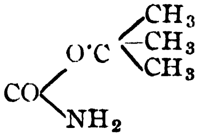
$$\mathrm{CO}\left\langle\begin{matrix}\mathrm{O{\cdot}C_2H_5}\\\mathrm{NH_2}\end{matrix}\right.$$

(III)



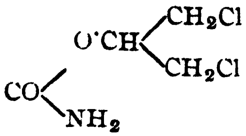
$$\mathrm{CO}\left\langle\begin{matrix}\mathrm{OCH}\left\langle\begin{matrix}\mathrm{CH_3}\\\mathrm{CH_2{\cdot}CH_2{\cdot}CH_3}\end{matrix}\right.\\\mathrm{NH_2}\end{matrix}\right.$$

(IV)

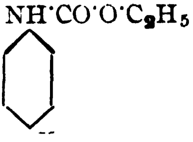


$$\mathrm{CO}\left\langle\begin{matrix}\mathrm{O{\cdot}C}\left\langle\begin{matrix}\mathrm{CH_3}\\\mathrm{CH_3}\\\mathrm{CH_3}\end{matrix}\right.\\\mathrm{NH_2}\end{matrix}\right.$$

(V)

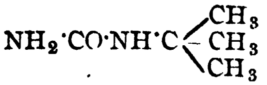


(VI)

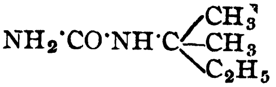


(VII)

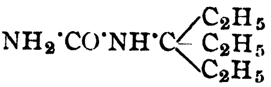
Concerning the higher aliphatic derivatives of urea a generalisation may be made somewhat similar to that which applies to the active amides namely, that the branched chained compounds are invariably more narcotic in their action than those with normal chains and that a tertiary formation containing a preponderance of ethyl groups favours the development of narcotic activity. Thus, *ter*-butylurea (VIII) is a compound with slight narcotic properties, while the *ter*-amylurea (IX) in which one of the methyl groups has been replaced by an ethyl group produced a ten-hours' sleep in the same animal in a dose of two grams. The replacement of all the methyl groups by ethyl groups as in the *ter*-heptylurea (X) gives a more powerful compound of which 1 g. only was required to produce a six-hour's sleep. It will be remembered that the three alcohols containing the *ter*-butyl, *ter*-amyl and *ter*-heptyl residues (XI—XIII) have also a hypnotic action, and that the



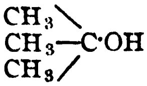
(VIII)



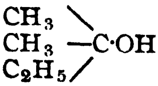
(IX)



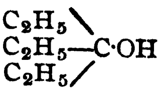
(X)



(XI)



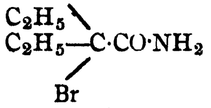
(XII)

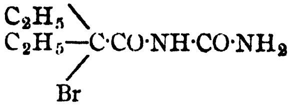


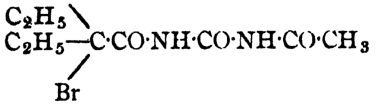
(XIII)

magnitudes of their activities are of the same relative order as those of the simple ureas.

The halogenation of acid amides and ureas almost invariably enhances their physiological activity. Among the first instances discovered of this action was that of the increase of activity obtained by brominating diethyl acetamide. The latter compound has only a moderate narcotic action, during a slight stupor, but bromodiethyl acetamide (Neuronal, XIV) has a comparatively strong narcotic action, producing a twenty-six hours' sleep. Similar increases in activity, not so pronounced however, are observed when ethylpropyl and dipropyl acetamide are converted into their bromine derivatives, whilst the acetyl derivative (XVI) of bromodiethylacetylurea (XV) has a hypnotic action superior to that of the parent body. It is to be noted, also, that the isomerof bromodiethyl acetamide – bromocaprylurea (XVII) is only one-fifth as active as that compound, a fact which further indicates the necessity of a tertiary hydrocarbon residue in building up hypnotics of this class.


(XIV)


(XV)

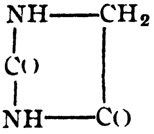

(XVI)

$NH_2{\cdot}CO{\cdot}NH{\cdot}CO{\cdot}C_5H_{10}Br$

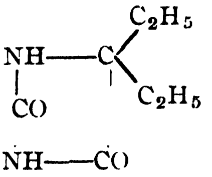
(XVII)

The bromination of valerylamide and its corresponding urea derivative also leads to the formation of compounds of enhanced activity. Thus, α-bromo*iso*valerylamide produces a fairly deep sleep, and α-bromo*iso*valeryl urea (Bromural) has been fairly used in practice Curiously enough, the lower members corresponding to these compounds, *e.g.*, α-bromomethylethyl acetylthiourea and α-bromo*iso*butyrylurea have but little hypnotic activity.

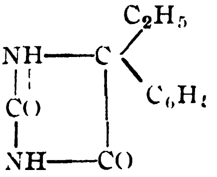
The question of the effect of the nature of the halogen atom upon the physiological action of compounds in this series, has been investigated in the case of the halogen compounds of *iso*valerylurea. *iso*Valerylurea itself has a comparatively slight narcotic action, but α-bromo*iso*valerylurea is a fairly good narcotic producing sleep. α-Chloro*iso*valerylurea is less narcotic. The introduction of iodine in place of chlorine, giving α-iodovalerylurea, appears to destroy almost completely the narcotic action. The simplest cyclic ureas are the hydantoins, concerning the physiological action of which but little is known. Hydantoin itself (XVIII) is physiologically inactive, and the γγ′-diethyl derivative, (XIX) corresponding to diethylacetylurea, possesses a certain narcotic action, which is nevertheless less than the last mentioned substance. The replacement of one of the ethyl groups by a phenyl residue greatly increases the narcotic activity and gives, in γγ′-phenylethylhydantoin (XX) a compound which by reason of its prompt narcotic working and freedom from unpleasant secondary effects is used in practice (Nirvanol).



(XVIII)



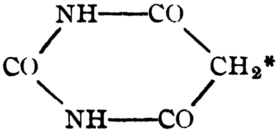
(XIX)



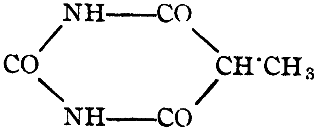
(XX)

The group of cyclic ureas which have been most widely investigated are the malonylureas, of which malonylurea itself (XXI) is the parent compound. The peculiar ease with which chemical derivatives of malonic ester can be prepared, accounts in some measure for the large number of members of this series of compounds which have been examined.

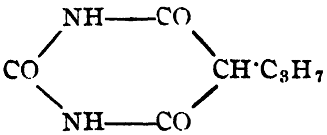
The narcotic action of malonylurea is insignificant, and can scarcely be said to exist. It is, however, a striking fact that a certain rough parallelism exists between the activity of the malonylureas and of the sulphones, especially in that the methylene group (*) must be elaborated up to a certain size by the substitution of its hydrogen atoms with alkyl groups before the narcotic activity becomes pronounced. Thus, the four compounds methyl,



(XXI)

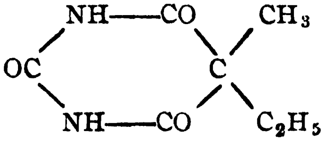


(XXII)



(XXIII)

(XXII) dimethyl, ethyl and propyl, (XXIII) malonylureas are all without any appreciable narcotic activity. The methylethyl derivative (XXIV) is, however, a mild narcotic, producing sleep, whilst diethylmalonylurea (XXV) (Veronal) is a powerful narcotic producing a deep sleep. The isomeric methylpropylmalonylurea (XXVI) is less active than the diethyl compound, producing only a mild stupor. There is no appreciable increase in narcotic effect when one of the ethyl groups of diethylmalonylurea is replaced by a propyl group, but the corresponding dipropyl compound (XXVII) is somewhat more active. Any increase in size of the carbon chains above that corresponding to two propyl groups is attended by a diminution in narcotic activity. Thus, di*iso*amylmalonylurea (XXVIII) produces only a kind of drowsy intoxication. The replacement of simple alkyl groups by unsaturated residues appears to produce only a slight increase in the narcotic activity compared with that of the corresponding saturated derivative. Thus, diallylmalonylurea (XXIX) (Dial) is almost equally as active as the dipropyl compound.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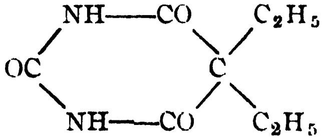
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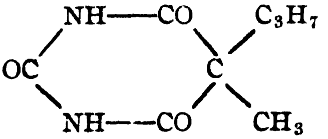
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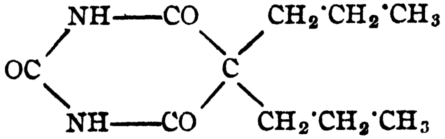
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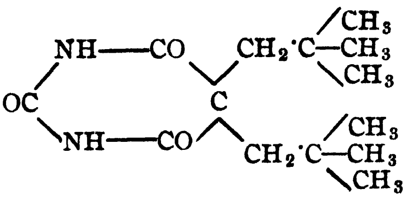
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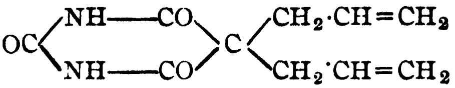
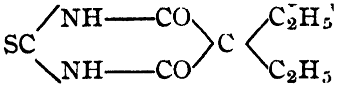


(XXIX)

The effect of various modifications in structure upon the activity of malonylureas shows that for the development of narcotic properties the structural type must be kept within comparatively narrow limits. Replacement of the oxygen of the urea group of diethylmalonyl urea by sulphur, as in thioveronal (XXX) does not appear appreciably to alter the hypnotic activity, although a considerable increase in toxicity is noticed. Methylation of the imino groups acts similarly, giving a fairly toxic compound, (XXXI), while the corresponding dibromopropyl compound (XXXIII) (Diogenal) finds use in practice as a rapid and powerful hypnotic.



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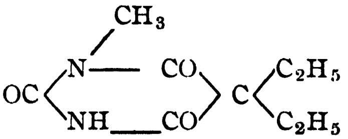
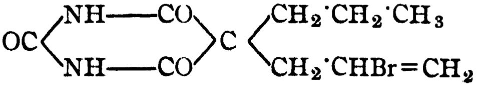
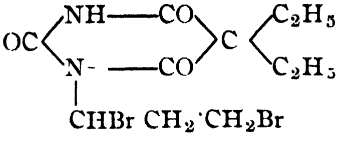


(XXXI)

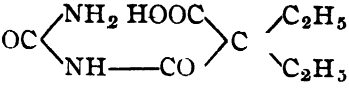
The use of a side-chain in which the bromine is attached to an unsaturated carbon atom has been found particularly active in developing the hypnotic activity of the malonylurea series. Thus β-bromopropenylpropylbarbituric acid (Noctal) (XXXII) has a powerful hypnotic action and produces a six-hour's sleep in proper doses.



(XXXII)



(XXXIII)



(XXXIV)

The opening of the ring malonyl is invariably associated with the almost complete inhibition of the narcotic activity. Thus, even with veronal, the corresponding open-chain compound diethylmalonic acid ureide (XXXIV) is quite inactive.

Amidopyrine.

Attempts to confer pain-relieving qualities on the barbiturates have not been very successful. The closest approaches to a solution which has been made up to the present are the association of a barbiturate nucleus with amidopyrine in Pfeiffer's compound, used in veramon, and the linkage with a member of the morphine group in Didial and Condeonal. Amidopyrine, a derivative of antipyrine, is well known under the registered name of Pyramidon, and appears to possess greater analgesic properties than antipyrine itself or other members of the coal-tar group. Its pain-relieving powers are enhanced by admixture with a simple hypnotic, possibly because the latter diminishes the patient's anticipation of pain. The fact has been made use of in a popular modern series of pain-relieving mixtures which fall outside the Dangerous Drugs Acts.

In each case pain-relief is due to amidopyrine combined rather mechanically or molecularly with a simple hypnotic. A barbitone derivative with pain-relieving qualities in its own right is still to be found.

Up to recent times, the derivatives of amidopyrine were considered to be of low toxicity. Recent observations have shown that they are responsible for an almost fatal condition known as agranulopenia. They have, therefore, to be used with very great caution.

The Margin of Safety in a Hypnotic.

The actual potency does not concern us much. It is just as easy to give five grains of one drug as one grain of a more potent one. The point of practical importance is the margin of safety between the hypnotic dose and the lethal one. This is represented by the ratio M. L. D./M. Th. D. The higher this figure, the safer the drug. Quoting from the literature : luminal is 1·3 ; barbitone 1·6 ; soneryl, nembutal and phanodorm, 2·4 ; dial, 2·5 ; evipan, 5. From this it would appear that it is not very safe to employ luminal in full hypnotic doses, although in sedative or anti-epileptic dosage it is free from immediate risk.

Duration of Sleep to be Expected.

The effect of a sleeping draught should last many hours, but die away before morning. For a basal anæsthetic a much shorter duration is desirable. Quoting once more from available literature :—Human therapeutic dosage : sodium evipan, intravenous, lasts twenty minutes and evipan by mouth, two hours. Rats with coma dosage : nembutal, four and a half hours, pernocton, five hours ; amytal, six to thirty hours ; barbitone, eighteen to thirty-six hours. The duration of narcosis produced by the dial group lies between the evanescent basal anæsthetics and that of drowsy barbitone itself. As judged by these two considerations of safety and duration alone the basal anæsthetics of choice are evipan and nembutal. Practical experience appears to justify this conclusion.

In 1927 a paper was read by Dr. F. A. Pickworth in which it was shown by animal experiments that actual degenerative changes occurred in the nerve-cells after the prolonged administration of barbituric acid compounds. This work had been carried out by the late Sir Frederiek Mott in conjunction with Dr. Pickworth. There is, therefore a pathological basis for the toxic nervous symptoms which are observed clinically.

In the stage of intoxication which precedes narcosis susceptible patients show excitement, which may hinder rather than promote sleep. The preventive for such trouble is a preliminary dose of bromide. In certain cases, therefore, bromine has been introduced into the barbiturate nucleus—for example, noctal, pernocton.

There are many urea derivatives other than the malonylureas, and some of them are first class hypnotics. They are not barbiturates, and are particularly useful for patients with idiosyncrasies and for those who have become habituated to barbiturates.

May I now refer to the hypnotic properties of the extracts from the root of *Rauwolfia Serpentina*. As early as March 1912, the speaker read a note on its alkaloidal principles and therapeutic properties in a meeting of the Asiatic Society of Bengal. The extracts have marked hypnotic properties and are specially indicated in certain forms of insanity. Since the above paper was read, much work has been done on the chemistry of the drug and many alkaloids have been extracted from the roots. Its hypnotic properties may be due to these alkaloids.

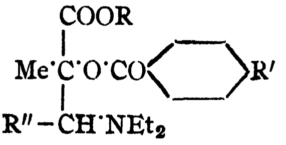
It would be more in keeping with the dignity and traditions of the profession of medicine and chemistry if independent pharmacological research could be endowed in our medical schools and universities sufficiently well to enable us to make our own discoveries. The credentials of every new hypnotic should be carefully examined before a single dose is prescribed.

Now I come to the end of my address and in doing so, I cannot help referring to the various accomplishments, the courteous and unassuming manners, the warmth and benevolence of heart which distinguish the gentleman who has been nominated by the Council to succeed me in this chair and I rejoice most sincerely that the Society possesses amongst its members a person who, is so well qualified to preside over our meetings, to watch over our interests and help us in our deliberations, and who has won for himself a high international reputation for his researches. May our Society prosper under the presidentship of Dr. J. C. Ghosh.

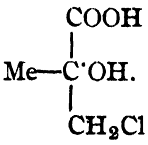
SYNTHESIS OF NEW LOCAL ANÆSTHETICS. PART I.

By K. N. Gaind.

Novy (*Amer. Chem. J.*, 1888, **10**, 145 ; also *cf.* Merck, *Ber.*, 1885, **18**, 2954; *ibid.*, 1888, **21**, 48) prepared different esters of benzoyl ecgonine and found that the higher the alcohol the more pronounced is the local anæsthetic property. Since the simplest compounds that can possess the local anæsthetic property are the benzoylated hydroxyamino acids, therefore it seemed of interest to synthesise substances possessing the general formula (I, R″=H), and vary R to find out if there is any change in activity.



(I)



$$\begin{array}{c} \mathrm{COOH} \\ | \\ \mathrm{Me{-}C{\cdot}OH.} \\ | \\ \mathrm{CH_2Cl} \end{array}$$

(II)

These have been prepared by converting monochloroacetone *via* its cyanhydrin to the corresponding chlorohydroxy*iso*butyric acid (II)

The acid was esterified with various alcohol (ethyl, propyl, *iso*propyl, benzyl), and then the chlorine atom was replaced by reaction with diethylamine under pressure. The hydroxyl group in (II) was benzoylated or *p*-nitrobenzoylated and in the case of the *p*-nitrobenzoyl derivative, the product was further reduced to *p*-aminobenzoyl derivative (I, R′=NH_2, R″=H) using the platinum oxide catalyst.

The cyanhydrin of chloroacetone, which could not be prepared satisfactorily by the method of Bischoff (*Ber.*, 1872, **5**, 865 ; *cf*, Fourneau, *Bull. Soc. chim.*, 1909, *iv*, **5**, 229), was obtained from the bisulphite addition product of chloroacetone by interaction with the calculated amount of potassium cyanide. The cyanhydrin was transformed to the corresponding hydroxy acid by fuming hydrochloric acid. The chlorohydroxy acid, thus obtained, was esterified with various alcohols.

Chloroethylmethyl ketone was prepared by the chlorination of ethylmethyl ketone (Forster and Fierz, *J. Chem. Soc.*, 1908, **93**, 675) and the two chloro compounds, Me·CH (Cl)·CO·Me and Me·CH_2·CO·CH_2Cl were separated by distillation in *vacuo*. The former was converted into its cyanhydrin and then hydrolysed. The resulting acid, Me·CH(Cl)·C(OH) (COOH)Me purified *via* its zinc salt, was esterified and then reacted with diethylamine and finally benzoylated giving (I, R″=Me, R′=H).

All the compounds described in this paper have strong local anæsthetic action as tested by rabbits' cornea method. A full detail of these experiments would be published elsewhere.

EXPERIMENTAL.

Freshly distilled chloroacetone (46 g.) was treated with a saturated solution of sodium bisulphite (54 g.) in small portions at a time and the rise of temperature was avoided by cooling in ice. The reaction was completed at 5° by allowing to stand for some time. A solution of potassium cyanide (65 g. in 130 c.c. of water) was slowly added to the mixture at 5° with stirring when the solids were replaced by an oily layer which was extracted several times with ether, dried, solvent recovered and then distilled, b·p· 110°/22 mm., yield 46 g. (*cf.* Bischoff, *loc. cit.*).

*β-Chloro-α-hydroxy*iso*butyric Acid.*—The foregoing nitrile (46 g.) was hydrolysed by fuming hydrochloric acid (60 c.c.), first at room temperature for 2 hours and then at 100° for 4-5 hours. The ester was isolated in the usual manner and crystallised from benzene, m.p. 110°. (*cf.* Fourneau, *loc. cit.*).

*Benzyl β-chloro-α-hydroxy*iso*butyrate.*—The above acid (13 g.) was esterified with benzyl alcohol (30 g.) with hydrogen chloride by heating at 100° for 12 hours. The ester, isolated in the usual manner, had b.p. 185°/45 mm. (Found : Cl, 15·45. $C_{11}H_{13}O_3Cl$ requires Cl, 15·52 per cent).

*Benzyl β-diethylamino-α-benzoyloxy-*iso*butyrate* (I, R=CH_2Ph ; R′=R″=H). A mixture of the above benzyl ester (20 g.), diethylamine (59 g. of 33% solution in benzene) was heated under pressure at 150° for 6 hours. The precipitated hydrochloride of diethylamine was separated and the benzene solution was freed from the solvent in *vacuo*. The residual oil was extracted with 2*N*-hydrochloric acid and the solution extracted with ether. The hydrochloric acid solution was concentrated and basified in the cold with sodium carbonate and extracted with ether. The ethereal solution furnished an oily base which decomposed on distillation in *vacuo*. Hence the crude base was directly benzoylated with benzoyl chloride and sodium bicarbonate solution. The benzoyl derivative was crystallised from hot dilute alcohol in needles, m.p. 63°. (Found: N, 3·9. $C_{22}H_{27}O_4N$ requires N, 3·79 per cent).

It was converted into the *hydrochloride* in dry ether with hydrogen chloride and purified by crystallisation from a mixture of ether and alcohol as slender needles, m.p. 198°. (Found : N, 3·5 ; Cl, 8·9. $C_{22}H_{28}O_4NCl$ requires N, 3·45 ; Cl, 8·75 per cent).

Hydrochloride of Benzyl β-diethylamino-α-(p-*nitro)-benzoyloxy*iso-*butyrate* (I, R = CH_2Ph ; R′ = NO_2 ; R″ = H).—A mixture of β-diethylamino-α-hydroxy*iso*butyrate (3 g.) and *p*-nitrobenzoyl chloride (3 g.) was heated at 160° for 1½ hours. The mixture was treated with dry ether and the insoluble residue was extracted with boiling acetone whence on concentration slightly brown needles, m.p. 190°, were deposited. The product was crystallised from a mixture of alcohol and ether, m.p. 195°. (Found : Cl, 8·0. $C_{22}H_{27}ON_2Cl$ requires Cl, 7·88 per cent).

Hydrochloride of Benzyl β-diethylamino-α-(p-*amino) benzoyloxy*-iso-*butyrate* (I, R = $CH_2.Ph$, R′ = NH_2 ; R″ = H).—The above compound (1 g.) in absolute alcohol (50 c.c.) was reduced using platinum oxide catalyst (0·1 g.) (*cf. J. Amer. Chem. Soc.*, 1922, **44**, 1397). After the removal of the solvent, the residue was crystallised from a mixture of alcohol and ether, m.p. 175°. (Found : N, 6·9 ; Cl, 8·5. $C_{22}H_{29}O_4N_2Cl$ requires N, 6·82 ; Cl, 8·46 per cent).

*Propyl β-chloro-α-hydroxy*iso*butyrate* had b.p. 100°/13 mm. (*cf.* Fourneau, "Organic Medicaments," 1925, p. 222).

The above ester was converted into the diethylamino derivative as described in the case of benzyl ester. The base in this case also resisted purification and therefore it was benzoylated as described before. The *propyl β-diethylamino-α-benzoyloxy*iso*butyrate* (delicate needles) melted at 56°. (Found : N, 4·3. $C_{18}H_{27}O_4N$ requires N, 4·36 per cent). The *hydrochloride* melted at 217°. (Found : Cl, 10·1. $C_{18}H_{28}O_4NCl$ requires Cl, 9·93 per cent).

The iso*propyl β-chloro-α-hydroxy*iso*butyrate*, prepared in an analogous manner, had b.p. 110°/12 mm. It was reacted with diethylamine and then benzoylated. The iso*propyl β-diethylamino-α-benzoyloxy*iso*butyrate* had m.p. 44° after crystallisation from dilute alcohol. (Found : N, 4·5. $C_{18}H_{27}O_4N$ requires N, 4·36 per cent). The *hydrochloride*, m.p. 207°, was crystallised from a mixture of alcohol and ether. (Found : Cl, 10·0. $C_{18}H_{28}O_4NCl$ requires Cl, 9·93 per cent).

α-Hydroxy-α-chlorovaleronitrile [Me·CH(Cl)·C(OH)(CN)·Me] was prepared from α-chloroethylmethyl ketone (not always homogeneous, *vide* below) *via* the bisulphite compound as described before.

The crude nitrile (5 g.) could be hydrolysed with fuming hydrochloric acid (30 c.c., *d* 1·26) by heating on the water-bath for 4 hours. After cooling the separated acids were extracted with ether and the residue from ether was converted into zinc salt by neutralisation with zinc carbonate.

The zinc salts were crystallised from hot water, the first crop being pure zinc salt of α-hydroxy-β-chlorovaleric acid, whence the acid, m.p. 92°. (*cf. Annalen*, 1890, **257**, 123) was isolated. In the case of benzyl ester, the tedious process of purification of the acid can be avoided by directly esterifying the crude nitrile. With benzyl alcohol, the resulting esters are separable by fractional distillation.

A mixture of the above nitrile (20 g.) and benzyl alcohol (60 g.) was saturated with hydrogen chloride at 0° and then heated at 100° for 5 hours. After decomposition with boiling water, the resulting ester (A) was extracted with ether, dried, and distilled at 180°/20 mm. A second ester (B), b.p. 210°/20 mm., may be admixed with the above if the chloroketone is not pure, presumably arising from an isomeric chloroketone.

The esters (A), and (B) when analysed gave Cl, 14·4 and 14·5 respectively. $C_{12}H_{15}O_3Cl$ requires Cl, 14·67 per cent.

The two esters were reacted separately with diethylamine and then benzoylated in the usual manner and the benzoyl compound derived from the ester (A) had m.p. 61° after crystallisation from alcohol, whilst the corresponding benzoyl derivative from (B) had m.p. 47°. (Found in A: N, 3·8 ; in B : N, 3·6. $C_{23}H_{29}O_4N$ requires N, 3·65 per cent).

The two hydrochlorides had m.p. 207° and 235° respectively [Found in the hydrochloride derived from the ester A: Cl, 8·5; and that from B : Cl, 8·4. $C_{23}H_{30}O_4NCl$ requires Cl, 8·46 per cent).

The author is inclined to the view that the ester (A) has the structure $Me·CH(Cl)·C(OH)(COOCH_2Ph)·Me$, whilst the ester (B) is probably $Me·CH_2·C(OH)(COOCH_2Ph)·CH_2Cl$. But at present definite proof is lacking for confirmation of the view. Both the hydrochlorides have strong local anæsthetic action.

The author's best thanks are due to the Lady Tata Memorial Trust for a scholarship and to Professors P. C. Guha and J. N. Rây for their kind interest and guidance.

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THE ELECTROCHEMICAL PROPERTIES OF PALMITIC ACID HYDROSOLS.

BY SUDHAMOY MUKHERJEE.

The study of the electrochemical properties of colloidal solutions of acidic substances has received considerable attention in recent years. Colloidal solutions are often treated as homogeneous systems possessing the properties of acids in true solution (Pauli and Valko, "Elektrochemie der Kolloide," 1929; Buchner, "Colloid Chemistry" by Alexender 1926, pp. 126-136). The work of Mukherjee and co-workers (a connected account of their work and references to literature have been given in a paper by J.N. Mukherjee, R. P. Mitra and S. Mukherjee, to be published shortly in the transactions of the National Institute of Sciences of India) on the other hand has drawn attention to their polyphase character and to the part played by the electrical double layer in such systems. Investigations on silicic acid sols and on acid clay sols have shown that interactions of these systems with electrolytes consist mainly of interchanges of ions present in the electrical double layer surrounding the particles. The present investigation on colloidal solutions of palmitic acid was undertaken with a view to examine its behaviour in the light of the above theoretical stand-points.

EXPERIMENTAL.

Preparation of Palmitic Acid Sol.—Pure palmitic acid (Kahlbaum) was dissolved in absolute alcohol (Merck's Reagent) so as to obtain a saturated solution The clear solution was added drop by drop to boiling conductivity water (specific conductivity $1{\cdot}3 \times 10^{-6}$ mho). Part of the palmitic acid, instead of being dispersed colloidally, floated on the surface in the form of solid particles. The sol was boiled for about 2 hours in order to drive off the alcohol. It was stocked, while hot, in the stocking vessel in an atmosphere of pure hydrogen. Fine sols without visible aggregates were obtained. The sol remained unchanged for about 10 days during which the measurements were made. On keeping for a longer period, aggregates begin to appear.

The stocking vessel.—The apparatus consists of a Jena glass bottle fitted with a normal burette by a ground-glass joint. It is so devised that the sol can be stocked and transferred in an atmosphere of hydrogen gas without coming in contact with atmospheric air. The sol comes in contact only with Pyrex and Jena normal glass surfaces and the system of glass apparatus is able to stand a vaccum of 75 cm. of mercury without showing any leakage. The arrangement is the same as described by Mukherjee and co-workers (*Indian J. Agric. Sci.*, 1932, **2**, 638 ; 1936, **6**, 577).

The titration Cell.—The titration cell is of the same type as described by Mukherjee and co-workers (*loc. cit.*).

Potentiometric Measurements.—A Cambridge potentiometer reading up to 0·2 milli-volt and a Leeds and Northrup galvanometer of high current sensitivity (4×10^{-11} amp.) were employed. The normal calomel half cell was used as the reference electrode.

Conductivity Measurements.—The source of A. C. was a Vreeland oscillator working at 500 and 1000 cycles per second. A recalibrated Curtis coil resistance box and a Leeds and Northrup marble drum bridge were used in the assembly. An air condenser of adjustable capacity was connected in parallel with the resistance box in order to balance the capacity of the cell.

Precautions against Electrical Leakages.—For preventing electrical leakages, which are often very troublesome, the following precautions were taken : (*a*) The experimental table was covered with an earthed metal sheet. (*b*) All electrical connections were made with lead covered Henley wires, the outer covers being earth connected. (*c*) All exposed terminals, etc., were protected with insulating tapes and covered wrth earthed copper gauze.

The Hydrogen Generator.—Hydrogen gas was obtained by the electrolysis of caustic soda solution in a U-tube with platinum electrodes. The gas was purified by passing through concentrated sulphuric acid, soda lime, then through a tube containing copper gauze heated in an electrical furnace (400°), and through purest soda lime and conductivity water, and finally through the experimental liquid before it passed into the titration vessel.

All the measurements were carried out in a water thermostat provided with an electrical heater and thermoregulator at a tememperature of 35° + 0·04°

RESULTS AND DISCUSSION.

Absolute Value of the p_H of the Sols.

It has been observed with silicic acid sols (*loc. cit.*) that the p_H values of the sols as obtained from the E.M.F. of the hydrogen electrode sometimes show irregular variations. Cleansing and replatinisation of the electrodes sometimes, though not always, improve matters. The difference in the initial values, however do not materially affect the determination of the total acidity from the titration curves. Similar irregular variations of the initial p_H have been observed also in the case of palmitic acid sols. The p_H was in some cases measured with the quinhydrone electrode for comparison. In the following table are given the observed p_H values for some of the sols on different days. In this table E has the same significance as in the equation,

$$p_H = \frac{E}{0{\cdot}0001984\ T} \qquad \ldots \quad (i)$$

for both the hydrogen and quinhydrone electrodes. The E.M.F. of the normal calomel half cell against the normal hydrogen electrode has been taken to be 0·2823 volt at 35°.

TABLE I

Sol A

	p_H		E	
	Pt_{H_2}	Q_H	Pt_{H_2}	Q_H
	5·28		0·3226	
		5·22		0·3189
	5·34		0·3263	
	5·34		0·3263	
	5·23		0·3195	
	5·25		0·3208	
	5·11		0·3122	
	5·19		0·3171	
Mean	5·26		0·3171	

Sol B

	p_H		E	
	Pt_{H_2}	Q_H	Pt_{H_2}	Q_H
	4·92		0·3006	
		4·78		0·2929
	5·00		0·3055	
	4.08		0·2993	
		4·77		0·2914
	4·97		0·3037	
		4·61		0·2817
	4·70		0·2872	
Mean	4 88	4·72	0·2981	0·2883

Sol C

	p_H		E	
	Pt_{H_2}	Q_H	Pt_{H_2}	Q_H
	5·48		0·3348	
	5·45		0·3330	
	5·10		3·3116	
	4·94		0·3019	
	4·91		0·2990	
	5·15		0·3147	
	5·25		0·3195	
	5·085		0·3107	
Mean	5·17		0·3160	

Sol D

	p_H		E	
	Pt_{H_2}	Q_H	Pt_{H_2}	Q_H
		5·10		0·3116
		4·90		0·2994
	5·00		0·3055	
	5·00		0·3055	
	5·07		0·3098	
Mean	5·023	5·00	0·3069	0·3055

The p_H of these sols is near about 5·0. It appears that the p_H (for sols A, B and C) gradually tends to diminish with time and reaches a value in the neighbourhood of 5·0. The maximum difference between the mean p_H values obtained with the hydrogen and quinhydrone electrodes is 0·16 p_H unit representing a difference of 10 m. volts. In the mojority of cases, the variations of the individual values of *E* obtained with the hydrogen electrodes from the mean values, do not exceed 5 m. volts, except in sol C, where the variations are generally larger. While the agreement should be considered satisfactory for such systems it is desirable to obtain E.M.F. values reproducible within 0·1 to 0·5 m. volt, as otherwise the calculated activity is liable to a large error.

For checking the reliability of the experimental arrangement and of the electrodes, a number of measurements were made in HCl solutions of several concentrations. The following table gives the observed p_H values and the values of *E* as defined above. The third column gives the difference in the values of *E* for the hydrogen and quinhydrone electrodes.

TABLE II.

	E		Diff. in m. v.	p_H	
	Pt_{H_2}	Q_H	$E_{Pt_{H_2}} - E_{Q_H}$	Pt_{H_2}	Q_H
(1)	0·1301	0·1289	1·2	2·129	2·11
(2)	0·1777	0·1793	1·6	2·908	2·935
(3)	0·1845	0·1839	0·6	3·02	3·01
(4)	0·2447	0·2428	1·9	4·005	3·974
(5)	0·2477	0·2497	2·0	4·054	4·087
(6)	0·2517	0·2533	1·6	4·12	4·08
(7)	0·2609	0·2593	1·6	4·27	4·26
(8)	0·3031	0·3018	1·3	4·96	4·94

In two instances, a difference of about 3 m.v. was observed between the two electrodes. It will be seen that with the precautions which have been adopted, the hydrogen electrode is fairly satisfactory. The larger variation of the p_H of the sols should perhaps be attributed to the difficulties in the attainment of equilibrium with hydrogen gas and the hydrogen ions on the surface of the electrode when the latter is immersed in the sol.

Titration of Palmitic Acid Sols with Bases.

Figures * 1, 2 and 3 show the titration curves of palmitic acid sol A with ammonia (curves 1 and 1′, Figs 1 and 2), caustic soda (curves 2 and 2′, Figs. 1 and 3), calcium hydroxide (curve 8, Fig. 1) and baryta (curves 4 and 4′, Fig. 1). The potentiometric and conductometric titration curves of sol B (curves 5 and 5′) with baryta are given in Fig. 5.

FIG. 1.

Palmitic acid sol A.

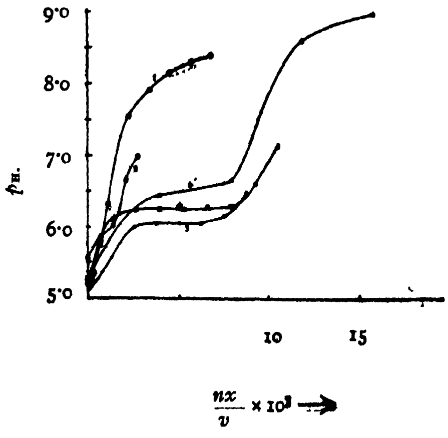
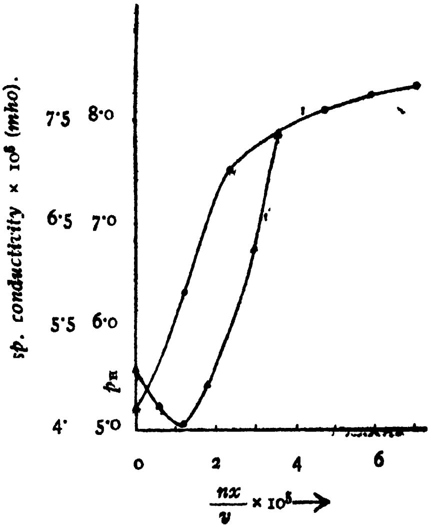


FIG. 2.

Palmitic acid sol A + ammonia.



The shapes of the potentiometric titration curves as well as the values of the total acidity calculated from the inflexion points in these curves vary with the base employed for the titration. The total acidity values of sol A calculated from the curves are given in Table III.

TABLE III.

Total acidity in normality × 10^5.

NH_4OH.	NaOH.	$Ba(OH)_2$.
1·2 (curve ** 1 or 1′)	1·9 (curve 2)	10·5 (curve 4)

---

* In these and in subsequent figures the abscissæ represent nx/v where n is the concentration of the electrolyte in normality, x its volume added and v, the resulting volume (initial volume $+x$) of the titrant.

** It is not possible to calculate the total acidity accurately from the potentiometric curve. This value has been calculated from the minimum point in the corresponding conductometric titration curve as this appears to agree with the inflexion point in the potentiometric curve.

In the potentiometric titration curves with caustic soda, calcium hydroxide and baryta, an initial rise of p_H is followed by a region of buffer action and then by a second steep rise. The point of inflection in the final rising portion has been used for calculating the total acidity. Beyond the inflexion point, the slope of the curve gradually diminishes. The buffering observed in the titration curves for calcium hydroxide and barium hydroxide is very strong and occurs between p_H 6·0 and 6·5. In the curves 3 and 4 (Fig. 1) the slope vanishes altogether in this region. In the curve for caustic soda, the region of buffer action is much shorter and occurs near p_H 6·0. The indication of a strong buffer action is altogether absent in the case of ammonia. In this curve (no. 1) a weak inflexion is observed at p_H about 6·3 and then the p_H rises sharply to about 7·5. The slope of the curve thereafter rapidly diminishes showing a strong buffer action.

Curves 3 for calcium hydroxide and curve 4 for baryta are of the same nature and run almost parallel. Their displacement appears mainly to result from the difference in the initial p_H values and the hydrogen electrodes in the two cases appear to have maintained a nearly constant difference of potential during the titrations. Curve 4 in Fig. 1 represents a titration which was carried out with larger additions of baryta, keeping the interval between the successive additions constant. The higher slope in the middle portion indicates a non-attainment of equilibrium with the added base.

FIG. 3.

Palmitic acid sol A+KOH.

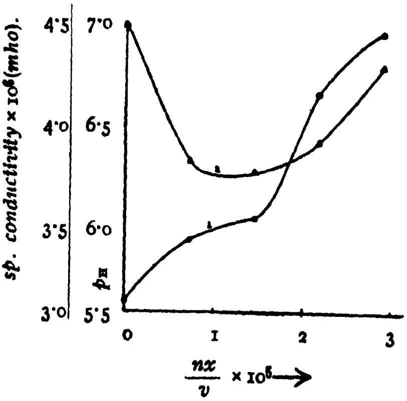
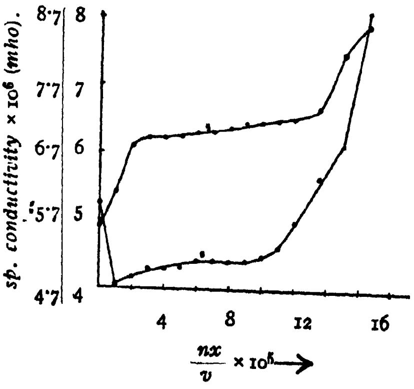


FIG. 4.

Palmitic acid sol B+baryta.



On titrating sol A with a concentrated solution of caustic soda (curves 6 and 6′, Fig. 5) the middle flat portion of the curve is completely suppressed on account of the larger additions of the alkali.

The conductometric titration curve of sol A with ammonia (Curve 1′, Fig. 2) has a fairly sharp minimum which agrees with the point of inflexion (not very sharp) in the potentiometric curve. With caustic soda, the conductometric curve has a rounded minimum (curve 2′, Fig. 9). This rounded portion corresponds with the region of buffer action in the potentiometric curve. With baryta the conductometric titration curve (curve 5′, Fig. 4) has a sharp lowering and then a region of almost constant specific conductivity in agreement with the flat portion in the p_H curve (curve 5, Fig. 4).

Total Acidity as Calculated from the Titration Curves and the Stoichiometric Content of Palmitic Acid in the Sol.

The palmitic acid contents of two sols have been compared with the titrable acids in the sols as calculated from the titration curves (*vide* Table IV). The palmitic acid was extracted from the sol with ether (100 c.c. of ether to 500 c.c. of the sol) and was weighed after evaporation to drynesss in a vacuum desiccator.

TABLE IV.

	Total acid ($N \times 10^5$) (By titration with baryta).	Palmitic acid ($N \times 10^5$) (By extraction).
Sol E	19·0	21·9
Sol F	16·2 14·3 Average = 15·2	15·0

Considering the small quantities of acid involved in the extraction, the agreement between the two sets of values should be regarded as satisfactory. In the titrations with baryta practically all the palmitic acid has thus reacted with the base at the inflection point.

Titration and Back Titration.

Palmitic acid sol C was titrated with baryta up to p_H 8·34 (beyond the point of inflexion which occurs near p_H 7·0) and then the sol was left overnight in the titration vessel after carefully sealing up with pure paraffin wax all openings of the titration cell so as to avoid ingress of carbon dioxide from the air. The next morning the sol was titrated with hydrochloric acid (curves 7 and 7′, Fig. 6).

FIG. 5.

Palmitic acid sol A+KOH

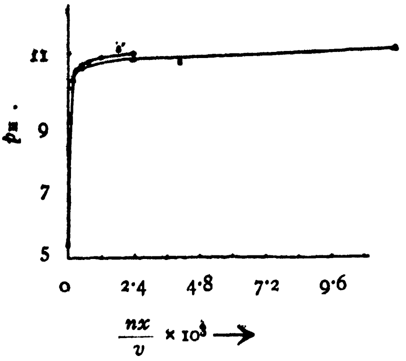
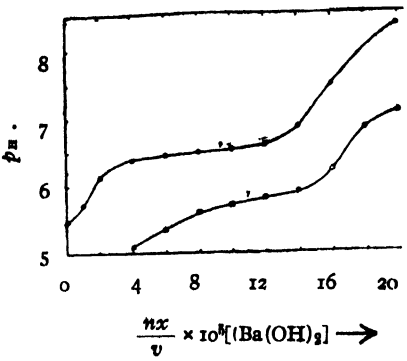


FIG. 6.

Palmitic acid sol C



The initial p_H on the second day was only 7·05. As the leakage of carbon dioxide in the cell is not likely, the lowering of p_H should be ascribed to a slow reaction with the excess of baryta. The back titration curve (curve 7', Fig. 6) has nearly the same form as the original titration curve and shows a striking parallelism with it. The back reaction, *viz.*, the formation of palmitic acid and barium chloride by the action of hydrochloric acid on barium palmitate is also attended with buffer action. The original reaction is thereby shown to be reversible. It may be mentioned that the sol had coagulated on standing overnight in excess of baryta. It is significant that the titration curves of the colloidal solution (baryta titration) and of the suspension of the coagulum (back titration with HCl) which certainly constitutes a heterogeneous system show such close resemblance.

Effect of Neutral Salts.

Palmitic acid sol B was titrated with potassium chloride and sol C with barium chloride (curves 8, 9 and 9', Fig. 7) and sol D also with barium chloride* (curve 11, Fig. 8). A similar titration of a hydrochloric acid solution of approximately the same p_H as the sol with barium chloride was carried out for comparison (curves 10, Fig. 7).

Potassium chloride produces only a slight change of p_H (0·04 p_H unit on the first addition, nx/v=0·002N) and on further additions, the p_H remains practically unchanged. Barium chloride on the other hand produced a larger change of hydrogen ion activity. The lowering of p_H is sharper at the beginning but the rate of change diminishes with increasing concentration of the added salt. In each of the barium chloride curves, a break in the slope is observed which suggests that the reaction occurs in two stages. The position of the break, however, appears to bear no relation to the hydrogen ion concentration of the sol or its palmitic acid content.

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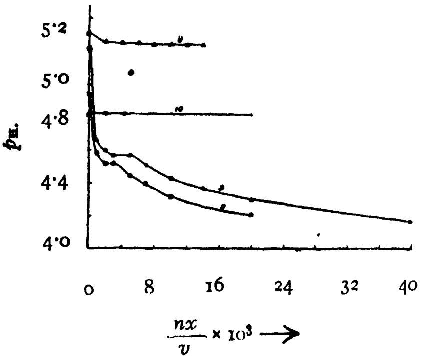
* This titration was stopped after the p_H came down to 4·44 and the titration cell was kept sealed overnight. On resuming the titration on the next morning, the p_H was found to be 4·16 and did not change on further additions of the salt.

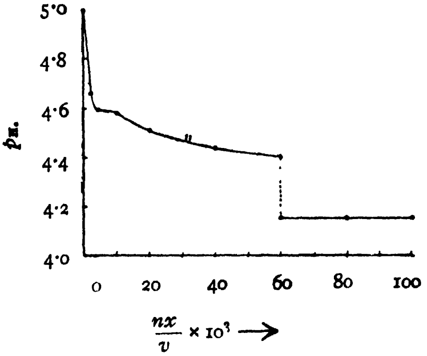
FIG. 7.



[Curve 8 refers to sol B + KCl; 9 & 9′ to sol C + $BaCl_2$ and 10 to HCl + $BaCl_2$ respectively.]

FIG. 8.

Palmitic acid sol D + $BaCl_2$.



Sols D and G were mixed with barium chloride so as to make the sol decinormal with respect to the salt in each case and left overnight. The mixture was titrated with baryta the following day. The titration curves of the two sols and of their mixtures with barium chloride are given in Figs. 9 (curves 12 and 13) and in Fig. 10 (curves 16 and 17).

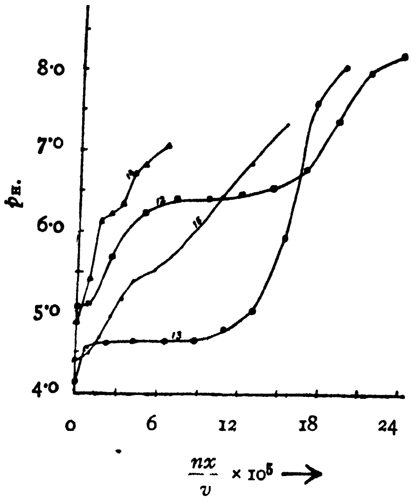
The shapes of the titration curves in the presence of barium chloride resemble that of a strong acid and have steeper inflexions.* The titration curves of the ultrafiltrates of sols D and G (curves 14 and 18) and of their ultrafiltrates in the presence of 0·1 *N* barium chloride (curves 15 and 19) are also given in the above figures. Curves 14 and 15 show buffer action between p_H 5·4 and 6·4. A thin ultrafilter membrane of finer pore size

* At the beginning of curve 11, there is a short flat portion and in the curve 12 a short rise in the same region. These features are absent in the curves for sol G.

was used for sol G with the result that this feature is absent in the titration curves (18 and 19) of the ultrafiltrates. It appears that in the former case, the ultrafiltrates contained fine colloidal particles of palmitic acid which had passed through the membrane.

Fig. 9.

Palmitic acid sol D.



The effect of the addition of barium chloride to palmitic acid sols on their free and total acidities and on those of their ultrafiltrates will be seen in Table V.

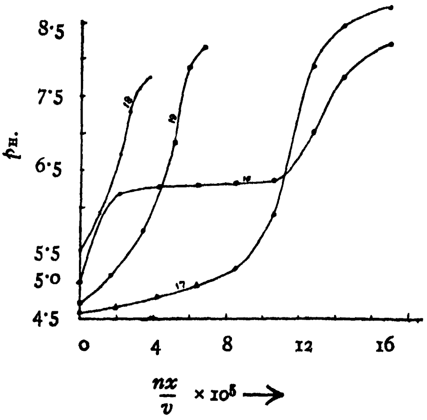
TABLE V.

	Without addition of salt			In the presence of 0·1 N-$BaCl_2$		
	p_H.	$a_H \times 10^5$.	Total acidity ($N \times 10^5$).	p_H.	$a_H \times 10^5$.	Total acidity ($N \times 10^5$).
Sol D	5·02	9·98	19·5	4·14	7·24	16·5
Ultrafiltrate	4·87 ?	—	3·5	4·40	3·68	9·0
Sol G	5·17	0·676	12·8	4·64	9·29	11·7
Ultrafiltrate	5·43	0·372	2·3	4·70	2·00	5·7

The total acidities of the sols in presence of barium chloride are somewhat less than those of the pure sols. The hydrogen ion activities of the sols in presence of barium chloride, though higher than those of the pure sols, are less than the total acidities of the sols (37% in the case of sol D and 18% in the case of sol G of their respective total acidities). This shows that at this stage the majority of the hydrogen ions are not free, *i.e.* are osmotically inactive, although they can react with hydroxyl ions at a lower p_H level (*vide*, curve 17) than in the pure sol.

FIG. 10.

Palmitic acid sol G.



Palmitic Acid Sol as a Single Phase System.

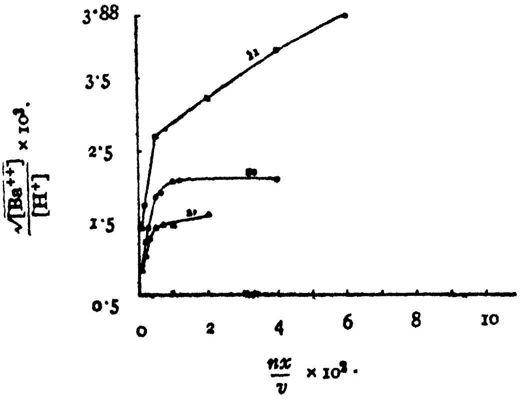
The point of view that colloidal solutions can be treated as single phase systems appears at first sight to receive support from the titration curves of palmitic acid sols, especially with the alkaline earth hydroxides, which resemble to some extent those of weak monobasic acids with a strong alkali. It will be shown below that the resemblance is only superficial.

Variations of the Total Acidity and the Difference in the Forms of the Titration Curves obtained with Different Bases.

It has already been pointed out that the total acidities calculated from the points of inflexion of the titration curves vary with the base employed.

Iyer (*Half yearly J. Mysore Univ.*, 1932, 6, 1) found a similar difference between the potentiometric titration curves of stearic acid hydrosols with caustic soda and baryta. In the titration of a weak acid with caustic soda which results in the formation of a soluble salt, part of the added alkali will remain unneutralised on account of hydrolysis and the p_H will rise initially. The dissociation of the remaining acid will be depressed due to the increased concentration of the anions and the 'buffer capacity' of the system will increase reaching a maximum value at the point of half neutralisation. The titration curve will thus have a comparatively flat middle portion. But the final point of inflexion will occur when the acid is completely neutralised and this point, as a result of hydrolysis, will lie in the alkaline region. The observed difference in the total acidity values with different bases is not expected of a truly dissolved acid when the resulting salts are soluble. Besides, the point of inflexion in the titration curve with caustic soda lies below p_H 7·0.

FIG. 11.



If we regard palmitic acid sol as a single phase system, its neutralisation with baryta or calcium hydroxide, which form insoluble salts with palmitic acid, should resemble the analogous case of the neutralisation of dissolved citric acid with calcium hydroxide. The insoluble calcium citrate formed during the titration separates out as a solid phase and the hydrogen ion concentration of the solution at any stage is determined by the concentration of the citric acid left unneutralised. No sudden rise of p_H should therefore be observed during the titration until at the equivalence point the p_H rises sharply similar to what happens on the addition of calcium hydroxide to pure water. The observed forms of the titration curves are not in agreement with the expected behaviour. Further evidence will presently be given against the hypothesis, that the colloidal solution of palmitic acid behaves as a single phase system.

Variability of the Dissociation Constant Calculated from the Titration Curves.

In the dissolved state palmitic acid is known to be a weak acid. The homologues of acetic acid up to decoic acid have dissociation constants not differing greatly from that of acetic acid, *viz.*, $1{\cdot}7 \times 10^{-5}$. McBain and Buckingham (*J. Chem. Soc.*, 1927, 2688) has assumed the value 10^{-5} for the dissociation constant of palmitic acid at 90° for making approximate calculations.

The values of a, the ratio of free acidity and total acidity, for a number of palmitic acid sols calculated from the equation :

$$K = \frac{a^2 c}{1 - a} \qquad \ldots \quad (ii)$$

are given in Table VI. The total acidities used in the calculations are those obtained from the potentiometric titration curves with baryta. The dissociation constants calculated from equation (*iii*) and from the titration curves at the points of one fourth, half and three fourths neutralisations using the Henderson equation :

$$p_H = p_k + \log\frac{[\text{Salt}] + [A]}{[\text{Acid}] - [A]} \qquad \ldots \quad (iii)$$

are also given in the same table.

TABLE VI.

	Acidity $(N \times 10^5)$		$K \times 10^7$				
	Free.	Total.	From eqn.		At 1/4 neutralisation.	At 1/2 neutralisation.	At 3/4 neutralisation.
Sol A	0·575	10·5	5·48	3·4	1·95	3·39	17·0
Sol B	1·59	14·6	10·9	19·5	1·95	4·79	10·0
Sol C	0·851	15·3	5·54	5·90	1·41	3·16	8·51
Sol D	0·980	18·8	5·21	5·30	1·95	4·47	8·91
Sol E	0·589	19·0	3·10	1·90	3·16	7·08	17·4
Sol F	0·631	15·3	4·13	2·66	1·86	4·57	11·5
Sol G	0·676	13·7	5·60	4·00	1·82	5·01	14·5

The calculated dissociation constants are mostly of the order of 10^{-7} and are lower than the probable value for the acid in the dissolved condition. The numerical values of K for the different sols, however, show large variations. Even for the same sol, the dissociation constant calculated from the titration curve increases steadily from the point of one fourth neutralisation to that of three fourths neutralisation. Such variation denotes that the rate of change of p_H in the titration curve is less than what should be expected in that of a weak acid in true solution.

In the potentiometric titration curve of a weak monobasic acid by a strong alkali, the slope of the curve at the point of half neutralisation has been shown by Auerbach and Smolczyk (*Z. physikal. Chem.*, 1924, **110**, 65), to be independent of the dissociation constant of the acid They obtain for the slope the expression

$$\frac{dp_H}{dx} = \frac{1{\cdot}74}{x_a} \qquad \ldots \quad (iv)$$

where x_a is the volume of the base required to reach the point of inflexion. Table VII gives the actual values of the slope at the point of half neutralisation in the titration curves with baryta and those calculated from equation (*iv*) for a number of sols. The slopes are expressed in terms of p_H units per c.c. of the added base.

TABLE VII.

	$\frac{dp_H}{dx}$ (obs.).	$\frac{dp_H}{dx}$ (calc.).
Sol A	0·375 0·00	1·58
Sol B	0·320	1·20
Sol C	0·150	1·16
Sol D	0·115	0·982
Sol E	0·537	1·83
Sol F	0·111	1·074
Sol G	0·078	1.36

The observed slope is always less than the calculated value of the minimum slope and is zero in curves 3 and 4 for sol A in Fig. 1. The titration curves thus show that the course of neutralisation of colloid solutions of palmitic acid is quite different from that of an acid in true solution.

Palmitic Acid Sol as a Two-phase System.

The behaviour of palmitic acid sol during titrations will be better understood if we regard it as a heterogeneous rather than a homogeneous system. The colloidal particles of palmitic acid may be regarded as constituting the solid phase in thermodynamic equilibrium with its saturated solution in water. On the addition of baryta to the sol there will be a lowering of the hydrogen ion concentration and a corresponding increase of the concentration of palmitate ions till the solubility product of barium palmitate is exceeded. The salt will now begin to form a second solid phase. The system will consist of three components existing in four phases (including the vapour) and will be univariant. At a constant temparature therefore (since the pressure may also be assumed to remain constant) the neutralisation should proceed at a constant composition of the system (Nernst, " Theoretical Chemistry," 10th German Ed., 1923, p. 626), *i.e.*, at a constant p_H. When one of the solid phases, namely, palmitic acid disappears, the system becomes bivariant and the p_H increases on the addition of the base. Since the salt is insoluble, there will be no perceptible hydrolysis and an inflexion will occur in the titration curve at the point of complete neutralisation of the acid at the neutral p_H. All these features are corroborated by the potentiometric titration curves 3 and 4 of palmitic acid sol A, where the titrations have been carried out under equilibrium conditions. The slight rise of p_H in the middle portions of the other curves must be attributed to the non-attainment of equilibrium with the added base. The only point of difference which is to be observed is that beyond the points of inflexions, the titration curves show indication of a reaction of the base with the insoluble salt.

On the addition of barium chloride to a palmitic acid sol, the insoluble barium palmitate is formed and simultaneously an equivalent amount of hydrochloric acid is liberated in accordance with the equation,

$$2\,HP + BaCl_2 = BaP_2 + 2HCl \qquad \ldots \quad . \ \ldots \qquad (v)$$

The system has now four components existing in four phases and is bivariant and at a constant temperature and pressure can remain in equilibrium with varying compositions of the liquid phase. Actually the p_H diminishes with increasing concentrations of barium chloride.

If S_1 and S_2 denote the solubility products of palmitic acid and barium palmitate respectively, the following relations follow from the law of mass action:

$$[H^+].\quad[P^-] = S_1 \qquad \ldots \qquad \ldots \qquad (vi)$$

and

$$[Ba^{++}].\quad[P^-]^2 = S_2 \qquad \ldots \qquad \ldots \qquad (vii)$$

whence

$$\frac{\sqrt{[Ba^{++}]}}{[H^+]} = S_2/S_1 = Z \text{ (constant)} \qquad \ldots \qquad (viii)$$

Thus, under equilibrium conditions the concentration of hydrogen ions should vary proportionately with the square root of the molar concentration of the barium ions in the solution. The values of Z calculated* at different points in the titration curves (curves 20 and 21 for sol C and curve 22 for sol D) with barium chloride are plotted against the equlvalent concentration of barium chloride nx/v in Figure 11. In each of the curves Z rises initially and after a break in the slope tends to become constant. In curve 20 it actually becomes constant after the addition of 0·01N-barium chloride with the exception of one stray value. In the other curves Z continues to increase, though slowly. That the variations of the value of Z indicate a true thermodynamic equlibrium between the different phases has not been established under these conditions.

The results given above show definitely that colloidal solution of palmitic acid differ in their electrochemical properties in some essential respects from acids in true solution. It has also been shown that the shapes of the titration curves with calcium hydroxide or baryta and the interactions of the sols with barium chloride are, barring some irregularities, in agreement with the expected behaviour if the colloidal solution be regarded as a heterogeneous system. The colloidal particles are to be considered as constituting a solid phase which is in equilibrium with its saturated solution. The irregular features are: (*a*) the slopes of the titration curves obtained with baryta at the point of half neutralisation are not always zero and (*b*) the value of the ratio $\sqrt{[B^{++}/H^{+}]}$ does not always ramain constant during the titration of the sol with barium chloride. The probable causes of these irregularities and also the mechanism of the interactions taking place between palmitic acid sols and bases and salts are discussed below.

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* In calculating these values the concentration of barium ions have been obtained by subtracting half of the increase of the hydrogen ions concentration of the sol from molar concentration of the barium chloride added to the sol. The assumptions have been made that (1) the observed increase in the number of hydrogen ions in the sol is accompanied with the disappearance of an equivalent number of barium ions from the solution and (2) the activity coefficient of barium chloride at the concentrations involved is unity.

It has been pointed out already in a previous section that a difference between the slopes of the titration curves of sol A with baryta is observed on changing the rate of addition of the base. It shows that the interactions taking place between the sol and the base are slow and the non-attainment of equilibrium under the conditions of experiment may lead to irregular results. There is another factor which may impart characteristic properties to colloidal solutions, namely, the electrical double layer surrounding the collodial particles (Mukherjee, Mittra and Mukherjee, *loc. cit*). The negative charge of colloidal particles of acidic substances originate from the existence of primarily adsorbed anions on their surface. An equivalent amount of hydrogen ions are present in the double layer, partly in the mobile condition and partly as secondarily adsorbed ions. Cations of an added electrolyte will displace the mobile hydrogen ions by diffusion into the double layer and may also get adsorbed on the surface and simultaneously displace the bound hydrogen ions. The ion pair formed by the metallic cation and the primarily adsorbed anion may or may not be stable on the surface depending on several factors. These factors are :—

(*a*) The lattice energy of the primarily adsorbed anions, *i.e.*, the forces holding these ions on to the neighbouring ions in the interior of the particles.

(*b*) The stability of the primarily adsorbed ions in the free state in solution.

(*c*) The solubility of the salt formed by the ions constituting the ion pair if it separates as a solid phase during the experiment.

(*d*) The lattice energy of the crystals of this salt. A relatively large lattice energy of the primarily adsorbed anions and a low stability of these ions in a state of solution would favour the formation of stable ion pairs on the surface, while under the reverse conditions the latter will split off from the surface and pass into the solution either as a dissolved molecule or forming a separate solid phase when its solubility product is exceeded. Again, a large difference between the lattice energies of the resulting salt and the primarily adsorbed anion or a low solubility of the salt will help the ion pair to pass into the solution. In the case where the ion pairs are stable on the surface, the electrical double layer and not the core of the particles is in equilibrium with the solution. The conditions underlying the classical phase rule are, therefore, not satisfied and the system behaves differently. On the other hand, if the ion pair passes into the solution as soon as it is formed, the colloidal particles as a whole takes part in the equilibrium and the colloidal solution behaves as a true heterogeneous system.

There is evidence to show that an electrical double layer exists surrounding the colloidal particle of palmitic acid. Mukherjee, Chaudhury and Bhabak (*J. Indian Chem. Soc.*, 1936, **13**, 379) have shown from microcataphoretic experiments that these colloidal particles are negatively charged. Wiegner and Pallmann ("Verhandlungen der zweiter Kommission und der Alkali Subkommission der internationalen Bodenkunlichen Gesellschaft," 1929, pp. 92-243) observed that suspensions of palmitic acid in water have higher hydrogen ion activities than the clear supernatant liquids. Again, it will be seen from Table V in this paper that the hydrogen ion activities of mixtures of sols D and G with 0·1*N* barium chloride are appreciably higher than those of their ultrafiltrates.* Such observations indicate that mobile hydrogen ions are present in the electrical double layer surrounding the colloidal particles. Here the primarily adsorbed ions are the palmitate ions. These ions are stable in alkaline solutions. In very weakly acid solutions they are stable at such a low concentration which obtains in the solution in equilibrium with the solid acid and barium palmitate. Besides, large differences between the lattice energies of solid palmitic acid and barium palmitate are also probable. On interaction with baryta, the ion pairs formed by the barium ions and the primarily adsorbed palmitate ions, therefore, split off as barium palmitate molecules and a separate phase is formed when the solubility product is exceeded. The system, as has been shown in a previous section, now behaves as a heterogeneous system obeying the phase rule and the law of mass action.

On the addition of barium chloride to the sol, the mobile hydrogen ions are displaced from the double layer and at the same time barium ions are adsorbed to form ion pairs. As in the titration of the sol with baryta, these ion pairs split off to form barium palmitate molecules as a separate phase and hydrochloric acid is liberated in accordance with equation(*v*). The increase in the concentration of hydrogen ions renders the palmitate ions less stable in solution and at the same time causes the displacement of the hydrogen ions on the surface by barium ions more difficult. Consequently the reaction with barium chloride remains incomplete. This is seen from the fact that the free acidity of the mixture of the sol with barium chloride is less than the total acidity of the sol. From the results so far obtained, it is difficult to decide whether in the interaction of palmitic acid sol with barium chloride a thermodynamic equilibrium between the acid and the salt in the solid phases is at all established. The non-uniform nature of the curves in Fig. 11 shows that the reaction is of a somewhat complex nature. Further work on this problem is in progress.

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* It will also be seen from Table V that sol G has a lower p_H than its ultrafiltrate but the reverse is observed in the case of sol D. The ultrafiltrates being extremely dilute unbuffered solution, the p_H values obtained for them are subject to a greater uncertainty than for the sols. Presumably in the above case the p_H of the ultrafiltrate of sol D is somewhat in error.

The lower value of the total acidity obtained by titrating a mixture of palmitic acid sol and barium chloride with baryta than that obtained by titrating the pure sol with the same base indicates that a portion of the acid remains unneutralised at the inflexion point in the former case. The sol coagulates in the presence of barium chloride and the aggregates probably enclose some of the acid molecules which are prevented from reacting with the added base by a layer of barium palmitate molecules covering the surface.

In the interaction of the sol with potassium chloride the mobile hydrogen ions are displaced into the intermicellary liquid but the adsorption of potassium ions does not proceed to any great extent on account of their low adsorbability. Again, potassium palmitate being soluble in water, the ion pairs formed will not appreciably pass into solution as the palmitate ions are unstable in such solutions at high concentrations. Consequently there is only a very small change in the hydrogen ion activity of the sol.

Ammonia being a weak base, ammonium palmitate is easily hydrolysed in solution. Ammonium ions are also relatively weakly adsorbed. Very little reaction is therefore indicated in the titration curve with ammonium hydroxide up to p_H 7·5. The strong buffer action which is observed above this p_H shows that palmitate ions are now stable and the neutralisation of the acid molecules proceeds. The colloidal particles gradually dissolve at this stage.

Sodium palmitate is stable and less hydrolysed than ammonium palmitate in solution. But it appears that the reaction is not strong enough below p_H 7 to dissolve the particles. The point of inflexion in the rising portion of the titration curve which also corresponds with the minimum of the conductometric titration curve, probably denotes the neutralisation of the dissolved palmitic acid in the sol. The p_H at the point of neutralisation gives an indication of the strength of the acid ($p_k = p_H = 7{\cdot}8$) in the dissolved condition. Further reaction of the colloidal particles with caustic soda takes place at a higher p_H level.

SUMMARY.

1. Irregular variations of the p_H of palmitic acid sols, measured with the hydrogen and quinhydrone electrodes, have been observed although the same experimental arrangement gives satisfactory results in dilute solutions of hydrochloric acid.

2. The forms of the electrometric and coductometric titration curves of palmitic acid sols and the total acidities calculated therefrom vary with the base employed for the titration. The latter vary in the order :

$$Ba(OH)_2,\ Ca(OH)_2 > NaOH > NH_4OH.$$

The total acidity obtained from the baryta titration curves agrees with the analytical concentration of palmitic acid in the sol.

8. The forms of the titration curves differ from that of an acid in true solution, whether the resulting salt is assumed to be soluble or insoluble. The calculated values of the dissociation constant are much lower than the probable value for the acid in the dissolved condition. The slopes of the titration curves with baryta at the point of half neutralisation are smaller than the theoretically calculated values for weak acids in true solution.

4. The titration curves with baryta and the interactions with barium chloride are, excepting some minor irregular features, in agreement with the expected behaviour assuming the sol to be a two phase system.

5. The mechanism of the interactions of colloidal particles of palmitic acid with different electrolytes has been discussed with reference to the electrical double layer surrounding the particles.

I take this opportunity to offer my sincere thanks to Prof. J. N. Mukherjee, D. Sc., for suggesting the problem and for his kind interest in the work. Thanks are also due to the Calcutta University for awarding me the Khaira Research Scholarship in Chemistry which enabled me to carry out this work.

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ON THE CONSTITUTION OF NITRO-β-METHYL-UMBELLIFERONE METHYL ETHER AND OF CHLORORESORCIN.

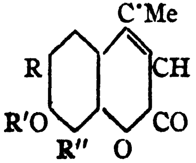
By Duhkhaharan Chakravarti and Bhowani Charan Banerji.

Pechmann and Obermiller* (*Ber.*, 1901, **34**, 666) observed that when β-methylumbelliferone methyl ether was nitrated in addition to 8-nitro-7-methoxy-4-methylcoumarin (I, R=H; R′=Me; R″=NO_2), m.p. 230°, another isomeric nitro compound, probably 6-nitro-7-methoxy-4-methylcoumarin (I, R=NO_2; R′=Me; R″=H), m.p. 281°, was isolated, the position of the nitro group being undetermined (*cf.* Beilstein, "Handbuch der organischen Chemie," Vierte Auflage, Band XVIII, p 33).

It is now found that 4-nitroresorcin (Borsche, *Annalen*, 1903, **330**, 106) condenses with acetoacetic ester producing 6-nitro-7-hydroxy-4-methylcoumarin (I, R=NO_2; R′=R″=H) in presence of sulphuric acid as the condensing agent. The presence of a nitro group greatly depresses the reactivity of the resorcin molecule in coumarin formation, since no product could be isolated by reacting 4-nitroresorcin with methyl- or ethyl-acetoacetic ester. It should be observed that the nitro group in position 4 has a more depressing effect than the nitro group in position 2 (*cf.* Chakravarti and Ghosh, *J. Indian Chem. Soc*, 1935, **12**, 622).

The constitution of the nitro-β-methylumbelliferone methyl ether, m.p. 281°, has been now proved to be 6-nitro-7-methoxy-4-methylcoumarin by its demethylation to 6-nitro-7-hydroxy-4-methylcoumarin, the condensation product of 4-nitroresorcin with acetoacetic ester.

The 6-nitro-7-methoxy-4-methylcoumarin has been reduced to the amino derivative, the diazo solution of which on treatment with cuprous chloride in hydrochloric acid gives 6-chloro-7-methoxy-4-methylcoumarin (I, R=Cl; R′=Me; R″=H),



The latter is found to be identical with the methyl ether of the condensation product of chlororesorcin with acetoacetic ester, thereby fixing the position

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* The work of Pechmann and Cohen, referred to by Chakravarti and Ghosh (*J. Indian Chem. Soc.*, 1935, **12**, 791) should be the work of Pechmann and Obermiller.

(4) of the chlorine atom in chlororesorcin. This constitutes further evidence in support of the position assigned to the chlorine atom in chlororesorcin by Clark (*J. Amer. Chem. Soc.*, 1933, **55**, 319) and by Chakravarti and Ghosh (*J. Indian Chem. Soc.*, 1935, **12**, 791).

EXPERIMENTAL.

6-Nitro-7-hydroxy-4-methylcoumarin.—A cold mixture of 4-nitroresorcin (5 g.) and acetoacetic ester (4 g.) was treated with sulphuric acid (*d* 1·84, 8 c.c.) drop by drop. The mixture was left for 2 days and then poured into ice water, the oil separating was washed with water and then with rectified spirit, when yellow crystals were obtained. These were recrystallised from glacial acetic acid (charcoal) as yellow needles, m.p. 255°. (Found : N, 6·28. $C_{10}H_7O_5N$ requires N, 6·3 per cent).

6-Chloro -7- methoxy -4- methylcoumarin.—(*i*) 6-Chloro - 7-hydroxy-4-methylcoumarin, the condensation product of 4-chlororesorcin with acetoacetic ester (Chakravarti and Ghosh, *J. Indian Chem. Soc.*, 1935, **12**, 622) was methylated by dimethyl sulphate in the usual manner. It was crystallised from glacial acetic acid as colourless needles, m.p. 252°. (Found: Cl, 15·6. $C_{11}H_9O_3Cl$ requires Cl, 15·8 per cent).

(*ii*) A solution of 6-amino-7-methoxy-4-methylcoumarin (1·5 g.) (Pechmann and Obermiller, *loc. cit.*) in hot concentrated hydrochloric acid (10 c.c.) was cooled in ice, when the hydrochloride separated as a fine precipitate. It was diazotised in the usual way and the diazo solution treated in the cold with a solution of cuprous chloride in hydrochloric acid. After standing for some time and subsequent heating on a water-bath for half an hour, 6-chloro-7-methoxy-4-methylcoumarin separated, which was collected, washed with hydrochloric acid and water and finally crystallised from glacial acetic acid as colourless needles, m.p. 251° (mixed m.p. with the compound prepared by the first method).

Demethylation of 6-Nitro-7-methoxy-4-methylcoumarin.—6-Nitro-7-methoxy-4-methylcoumarin (1·5 g.) was heated with aluminium chloride (4 g.) in an oil-bath, the temperature being gradually raised to 150° during the course of 3 hours. The brown solid obtained on treating with ice was dissolved in sodium hydroxide and the solution acidified. The flocculent brown precipitate was dried and crystallised from glacial acetic acid, m.p. 253°, the m. p. being not depressed when mixed with 6-nitro-7-hydroxy-4-methylcoumarin, the condensation product of 4-nitroresorcin with acetoacetic ester.

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CHEMICAL EXAMINATION OF THE ROOTS OF *ARISTOLOCHIA INDICA*, LINN. PART III. ISOLATION OF THE ALKALOID ARISTOLOCHINE.

By P. R Krishna Swamy and B. L Manjunath.

A brief summary of the reputed medicinal properties of the roots of *Aristolochia Indica* and of the chemical investigations on the principal members of the *Aristolochiacæ* is included in Part I of this series (*J. Indian Chem. Soc.*, 1935, **12**, 476). We have also indicated the occurrence of a crystalline alkaloid in *A. Indica* and proposed for it the name Aristolochine, which had been previously adopted by Pohl (*British Chem. Abs.*, 1892, I, 874) for the bitter toxic substances from *A. Rotunda* and *A. Clematitis*, and by Hesse (*Arch. Pharm.*, 1895, **233**, 684) for an amorphous alkaloid from *A. Argentina.*

We are indebted to Prof. J. L. Simonsen for suggesting the search for this alkaloid and the principal difficulty has been that in the large majority of the samples of roots from different parts of South India, the alkaloidal content is only 0·05—0·07 per cent and is nil in some of the roots obtained locally. However, during the course of the regular analysis described in Part I, sufficient alkaloid was obtained in a pure condition to enable its characterisation.

Aristolochine crystallises from methyl alcohol and melts at 215°. It has the formula $C_{17}H_{10}O_3N$ and it is interesting to compare this with that of *iso*aristolochic acid, $C_{17}H_{11}O_7N$, another constituent of the same roots. The base forms additive compounds with benzene and toluene, a property which is also exhibited by the cinchona alkaloids (Winterstein-Trier, "Die Alkaloide," 1931, p. 405).

We have now prepared a larger quantity of the alkaloid and are engaged in the investigation of its constitution.

EXPERIMENTAL.

Extraction and Isolation of the Alkaloid Aristolochine.—The crushed roots (50 kg.; alkaloidal content 0·05 %) were extracted with alcohol. The alcoholic extract was concentrated to a small bulk and treated with excess of dilute hydrochloric acid, when a considerable amount of the extracted material separated as a thick viscous mass. The aqueous layer was separated, treated with excess of ammonia and repeatedly extracted with chloroform. The chloroform solution was dried over anhydrous sodium sulphate, filtered and extracted with dilute hydrochloric acid. The acid solution was concentrated on a water-bath, treated with animal charcoal, filtered and again concentrated in a vacuum desiccator over solid sodium hydroxide. The hydrochloride gradually separated as a microcrystalline powder (Fig. 2) and was purified by recrystallisation from water. This was dissolved in water and excess of ammonia added, when the base separated as a curdy precipitate. This was filtered and dried. It was found advisable to crystallise it first from toluene when the base was obtained in the form of an additive compound.

This addition compound dissolved readily in methyl alcohol, but the free base separated out soon as a crystalline powder, yield 20 g. When crystallised again from methyl alcohol (Fig. 1) it melted at 215°, $[\alpha]_D^{25^\circ} = -268{\cdot}6^\circ$. [Found: C, 71·3, 71·4, H, 6·6, 6·6, N, 4·8, 4·9; M. W. (Kljatschkina *et al*, *Chem. Zentbl.*, 1932, I, 1376) 289, 292; $C_{17}H_{19}O_3N$ requires C, 71·6, H, 6·7; N, 4·9 per cent. M.W., 285].

FIG. 1.

Aristolochine

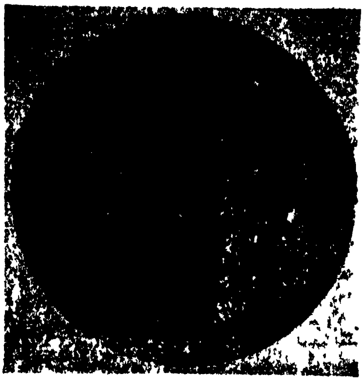

FIG. 2.

Aristolochine hydrochloride.

Properties of Aristolochine.—The hydrochloride melted at 268° (decomp.), $[\alpha]_D^{25^\circ} = -236{\cdot}2^\circ$. (Found: Cl, 11·2. $C_{17}H_{19}O_3N$, HCl requires Cl, 11·0 per cent). The hydrobromide melted at 262° and decomposed at

282°. (Found : Br, 21·5. $C_{17}H_{19}O_3N$, HBr requires Br, 21·8 per cent). Both these salts are fairly soluble in water. The addition compound with toluene melted at 159° (decomp.) [Found : C, 74·4; H, 7·1; N, 4·2. $(C_{17}H_{19}O_3N)_2$, C_7H_8 requires C, 74·3; H, 7·0; N, 4·2 per cent], and that with benzene melted at 163° (decomp.). [Found : C, 74·2; H, 7·0; N, 4·4. $(C_{17}H_{19}O_3N)_2 \cdot C_6H_6$ requires C, 74·1; H, 6·8; N, 4·3 per cent]. From this also, the free base could be generated by treatment with methyl alcohol.

The *picrate* was prepared by adding the requisite amount of picric acid, dissolved in methyl alcohol to methyl alcoholic solution of the alkaloid. It gradually separated out on cooling, but could not be recrystallised from any solvent. It was repeatedly washed with boiling alcohol. The dried material decomposed at 222°. The picrolonate, m.p. 232° (decomp.), was also prepared in the same manner, and it was possible to crystallise it from methyl alcohol.

Aristolochine is sparingly soluble in most of the common solvents. It dissolves readily in alkalis, but is precipitated on saturating the solutions with carbon dioxide. It does not give any colouration with ferric chloride. It is found to contain one methoxy group [Found : OMe, 10·7. $C_{16}H_{16}O_2N$-(OMe) requires OMe, 10·9 per cent], but no methylene-dioxy group (Hans Meyer, "Analyse und Konstitutionsermittlung organischen Verbindungen," 1931, p. 497 ; Sanchez and d'Alessio, *Chem. Zentrl.*, 1932, **II**, 257). It is unacted upon by boiling alcoholic potash or reagents for carbonyl groups, and contains only one reactive hydrogen atom (Zerewitinoff estimation, Found : 1·2 H-atoms). The nitrogen atom is found to carry two methyl groups when estimated according to the method of Haberland and Slotta (*Ber.*, 1932, **65**, 127) using Friedrich's micro-apparatus. (Found : NMe_2, 15·7. $C_{15}H_{13}O_3NMe_2$ requires NMe_2, 15·5 per cent).

The constitution of aristolochine as well as its pharmacological properties (the latter in the University Medical College, Mysore) are under investigation.

One of us (P. R. K. S.) is indebted to the University of Mysore for a Research Scholarship which enabled him to take part in this work.

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POTENTIOMETRIC ESTIMATION OF LEAD WITH SULPHIDE SOLUTIONS.

BY GOPAL LAL MAHESHWARI AND J. B. JHA.

Lead has been potentiometrically estimated by several methods; Muller and Gabler (*Z. anal. Chem.*, 1922, **62**, 28) used ferriferrocyanide electrode for its determination. The method is said to give good results for concentrations above 0·01*M*. This electrode has been investigated by Muller in collaboration with various authors for the titrations of lead in presence of various metals. Many of these methods require very precise conditions for successful results and hence their utility as working methods is limited (Muller and Pree, *Z. anal. Chem.*, 1927, **72**, 200; also Muller and Hentschel *ibid.*, 1927, **72**, 1). More recently Pamfilov and Ivanoeva (*J. Gen. Chem.*, 1931, **1**, 760) have used what they term bromopotentiometric method. Gelbachadd and Compton (*Ing. Eng. Chem. Anal. Ed.*, 1930, **2**, 397) have described a method with the use of thermionic valves. These authors have used potassium chromate solutions as the precipitant and the end-point is denoted by a minimum deflection on a milliammeter. Kolthoff and Furman (' Potentiometric Titrations," 1931, p. 187) have described a method with the use of sodium sulphide as precipitant and silver in 1·5*N*-KBr as a compensation electrode. The error in this case amounted to 1—2%.

Recently Mukai (*Bull. Tech. Coll. Kyushu Imp. Univ.*, 1929, **4**, 17) has applied the principle of the potentiometric titrations to the estimation of lead. Good results have been obtained with lead nitrate solutions only, with lead acetate solutions the results are irregular. Millet (*Trans. Faraday Soc.*, 1929, **25**, 147) has also shown that the concentrations of lead ions can be obtained by the E.M.F. measurements of lead in lead citrate solutions but his aim is not analytical as is evident from the perusal of his paper.

The titrations described below were carried out with hydrogen sulphide solutions and the method has the merit of being more accurate and simple. The whole titration can be performed within a few minutes, without the use of any mechanical device for stirring, etc. The method, however, is not suitable for solutions having concentrations greater than 0·02*N*, as it has been found difficult to increase the concentration of hydrogen sulphide for corresponding titrations. Moreover, hydrogen sulphide requires care in keeping and have to be standardised daily. The standardisation is not difficult and can be carried out with standard iodine solutions.

EXPERIMENTAL.

Lead Solutions.—Lead in the form of lead acetate dissolved in water with a little acetic acid to get a clear solution was used for estimation. To check the results of titrations lead was estimated gravimetrically as sulphate.

Sulphide Solutions.—These were prepared from sodium sulphide (B. D. H. A. R.) by dissolving it in a buffer solution consisting of equal volumes of sodium acetate and acetic acid solutions each 0·2*N*. The hydrogen sulphide solution was kept under hydrogen and used in the same way as titanous chloride solutions are used in reduction methods of titrations (Knecht and Hibbert, "Reduction Methods of Titration," 2nd Edition).

It may be pointed out here that the solutions keep admirably well under hydrogen. Photochemical action on the decomposition of hydrogen sulphide of the surface action due to glass seems to be slow. In one case no measurable change was observed after 30 hours.

Titration Vessel.—A special titration vessel was made out of a wide-mouthed bottle. A cork with three holes was fitted to the mouth of the bottle (250 c.c.). Platinum electrode, the connecting end of the calomel electrode and the lower end of the burette were inserted into these holes. A closed bottle for the titrations is necessary to check the loss due to diffusion, while the solution is flowing out of the burette.

The hydrogen sulphide solution was standardised by running out a known volume of the solution from the burette in a standard iodine solution containing a known amount of iodine. The excess of iodine was then titrated back with sodium thiosulphate solution of known strength.

The agreement between gravimetric and potentiometric results is given in Table I.

TABLE I.

Conc. of lead acetate soln. (approx.).	Conc. of H_2S soln. used (approx.).	Pb in lead acetate soln. found by gravimetric analysis (g./25 c.c.)	Pb found by potentiometric titration (g./25 c.c.)	Percentage error.
M/40	*M*/66	0·1054	0·1053	0·09
M/60	*M*/66	0·07645	0·0765	0·07
M/100	*M*/66	0·046915	0·02691	0·1
M/140	*M*/56	0·03416	0·03498	0·1
M/200	*M*/100	0·023457	0·023457	0·0
M/240	*M*/100	0·019114	0·01212	0·03
M/280	*M*/100	0·01708	0·01710	0·1
M/500	*M*/250	0·009380	0·009383	0·0
M/700	*M*/250	0·006832	0·006832	0·0
M/2000	*M*/250	0·002345	0·002345	0·0

E. M. F. variations during two titrations are given below.

The titrations were carried with a drop burette as suggested by Kolthoff and Furman (" Potentiometric Titrations," 1934, p. 84).

Concentrated solutions of lead acetate were prepared and the amount of lead estimated by the gravimetric method as sulphate. The solution was then diluted to the strehgths (approximate) given below.

TABLE II.

Lead acetate$=M/500$ (approx.)

Vol. of H_2S solution.	Pb pptd.	E. M. F. in volts against saturated calomel electrode.
0 c.c.	0.0%	−0·0400 volt.
5	76·55	−0·0210
6	91·66	−0·0380
6·112	...	−0·0450
6·224	95·3	−0·0300
6·336	...	−9·0590
6·382	...	−0·0650
6·45	...	−0·0750
6·50	99·58	−9·1000
6·55	...	−0·1450
6·60	101·3	−0·1720

Maximum$=\frac{de}{dc}$ at 6·53 c.c.

Quantity of lead found by potentiometric titration=0·009383 g./25 c.c.
Quanttty of lead found by gravimetric analysis=0·009313 g./25 c.c.
Percentage error=0%.

TABLE III

Lead acetate$=M/2000$ (approx.)

Vol. of H_2S soln.	Pb pptd.	E. M. F. against saturated calomel electrode.
0 c.c.	0%	+0·0520 volt.
8	69·2	−0·0040
9	77·92	−0·0120
10	86·58	−0·0170
11	95·24	−0·0300
11·2	96·97	−0·0420
11·3	...	−0·0580
11·4	...	−0·0680
11·46	...	−0·0740
11·51	99·59	−0·0900
11·55	...	−0 1400
11 60	100·45	−0·1550

Maximum$\frac{de}{dc}$ at 11. 535 c. c.

Amount of lead found by the above titration=0·002345 g. '25c.c.
Amount of lead found by the gravimetric analysis=0·002345 g./25c.c.
Percentage error=0%

It is clear from the above table that the method gives better results for more dilute solutions than for stronger ones.

The method is specially adopted for the estimation of lead in lead acetate solutions used in dyeing industry, where estimations are frequently required and are done with more tedious methods.

SUMMARY.

Potentiometric titration of lead with hydrogen sulphide solution has been described. The results have been found to be satisfactory for dilute solutions of lead acetate.

Our thanks are due to Prof. H. Krall, Head of the Chemistry Department and to Prof. B. L. Vaish for constant encouragement.

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A METHOD OF QUALITATIVE ANALYSIS WITHOUT THE USE OF HYDROGEN SULPHIDE.

By M. B. Rane and K. Kondaiah.

The obvious undesirability of the obnoxious and poisonous hydrogen sulphide gas as a necessary reagent in the chemical laboratory, induced many previous workers to devise alternative schemes of qualitative analysis avoiding its use. Fresenius ("Qualitative Analysis", 17th Ed, translated by Mitchell, pp. 836-849), gives the details of five such alternative methods, *viz*:—

(*i*) Schiff and Tarugi's thioacetate method

(*ii*) Vortmann's sodium sulphide method

(*iii*) Votmann's thiosulphate method

(*iv*) Ebler and Knoevenagel's method of separation by means of hydrazine and hydroxylamine salts

(*v*) Alinkvist's method using potassium hydroxide and potassium carbonate.

In these methods, however, sulphides of alkalis and other thio-salts, not less undesirable, are freely used. It was only recently that a method in which hydrogen sulphide in any form is specifically eschewed, has been worked out by O. Macchia (*Z. anal. Chem.*, 1927, **87**, 180). The method, however, is rather complicated and elaborate.

The present method, in which the bases are divided into five groups, gives a sharp and satisfactory separation and is expeditious. No special modification is needed even in presence of phosphates, oxalates, etc. The method has been verified in the laboratory by analysing a number of complex mixtures containing 10 or 12 bases and the results have been quite satisfactory. The scheme confined to the common base is outlined in Table I.

TABLE I.

Separation of the basic constituents into groups.

Treat the mixture with hydrochloric acid and evaporate with nitric acid : take up with nitric acid and filter.

Residue :—	**Filtrate + ammonium sulphate.**			
Ag, Sb, Sn and Insoluble matter	**Ppt. :— Ba, Sr, Pb, (Ca)**	**Filtrate :—Test for phosphoric acid. Add ammonia and ammonium phosphate**		
		Ppt. :—	**Filtrate :—Heat with NaOH**	
		Na, Al, Cr Mn, Bi, Ca, Mg (As)	**Ppt :— Co, Ni, Cu, Cd Hg**	**Filtrate : Zn & As—**
Group I.	Group II.	Group III.	Group IV.	Group V.

About 1 g. of the mixture is treated in a Casserole with 5-10 c.c. of 12*N*-hydrochloric acid, heated and then without filtering, boiled with 10 c.c. of 16*N*-nitric acid, evaporated to dryness, the residue treated with 5 c.c. more of the acid, warmed and filtered (*cf.* Note 1). The residue is washed with 6 *N*-nitric acid and treated as Group I. The filtrate is treated with 15-20 c.c. of a 20% ammonium sulphate solution, heated to boiling, allowed to stand a little, and filtered. The precipitate contains Ba, Sr (Ca) and Pb as sulphates. About 2 c.c. of the filtrate from above is tested separately in cold, with ammonium molybdate for the presence of phosphate (*cf.* Note 2).

Note 1. Experiments have shown that Sb_2O_4, formed under the circumstances, is practically insoluble in nitric acid 6*N* and above, though slightly soluble in acid of lesser cencentrations (*J. Indian Chem. Soc.*, 1936, **13**, 544).

Note 2. In presence of ammonium sulphate, the phosphomolybdate precipitate is thrown down readily in cold (distinction from arsenomolybdate which requires boiling for precipitation.

The rest of the solution is heated to boiling and a liberal excess of $6N$-ammonia is added until a strong smell persists, and then a hot solution of $1N$-ammonium phosphate until there is no further precipitation (*cf.* Note 3). The precipitate is treated as Group III (*cf.* Note 4).

The filtrate from the above is boiled with 15-20 c.c. of a $3N$-sodium hydroxide solution. The precipitate is washed with NaOH solution and treated as Group IV. Zn and As, forming Group V, are tested for in the filtrate from Group IV, while the alkalis are tested for in the original mixture.

GROUP I

Residue from hydrochloric and nitric acid treatment: Treat with $6N$ ammonium hydroxide, filter and wash.

- Residue :—Stannic oxide, antimony pentoxide and other acid insoluble matter. Treat with ammonium acetate and filter.
  - Residue :—Digest with 5-10 c.c. of 12 N-hydrochloric acid and filter.
    - Residue :—Acid insol. matter. Treat in the usual way.
    - Filtrate :—Chlorides of tin and antimony. Heat with reduced iron powder and filter.
      - Residue :—Black metallic antimony. Dissolve and confirm as usual.
      - Filtrate :—Stannous chloride. Confirm by $HgCl_2$ test.
  - Filtrate :—Test for lead with chromate.
- Filtrate :—Acidify with $6N$-nitric acid. White ppt. Ag.

GROUP II.

Treat the precipitate with 5—15 c.c. of $3N$-ammonium acetate and filter.

- Residue :—Boil with 25 c.c. of saturated sodium carbonate solution, with a pinch of the solid (Na_2CO_3). Decant through a filter and repeat the process.
  - Residue : Carbonates of Ba, Sr, Ca and Pb if any. Take up with nitric acid and remove lead by addition of NH_4OH and test the filtrate for alkaline earths as usual.
  - Filtrate :—Na_2SO_4 reject.
- Filtrate :—Test with potassium chromate. Yellow ppt. soluble in sodium hydroxide, Pb.

Note 3. Ammonium phosphate is added to precipitate here Ca, Mg. and Mn also.

Note 4. Ordinarily mercury is precipitated with ammonia and ammonium phosphate ; the presence of excess of ammonium sulphate, however, keeps it in solution.

GROUP III.

Precipitate : Hydroxides, phosphates or arsenates of Fe, Al, Cr, Bi, Mn, Ca and Mg.

Dissolve in 6*N*-hydrochloric acid, and treat with sodium carbonate and sodium peroxide and filter.

- Ppt. :—Fe, Mn, Bi, Ca and Mg Dissolve in 6*N*-nitric acid, with a little H_2O_2 if necessary; evaporate, and boil with 6*N*-nitric acid and potassium chlorate.
  - Ppt. :—Black MnO_2; confirm as usual.
  - Filtrate :—Add ammonium chloride and ammonia.
    - Ppt. :—Bi & Fe. Dissolve in HCl and add granulated zinc, heat and filter.
      - Residue : Black Bi; dissolve in nitric acid and confirm by alkaline stannite test.
      - Filtrate Fe. Oxidise, and confirm as usual.
    - Filtrate :—Ca, Mg. Separate test as usual
- Filtrate :—Aluminate, chromate, phosphate, arsenate of sodium Acidify with hydrochloric acid, test one portion for As, after reduction with SO_2, by Bettendorf test and add ammonia to the rest.
  - Ppt. :—Dissolve in sodium hydroxide and treat with barium chloride and filter.
    - Ppt —Barium phosphate, reject.
    - Filtrate :—Al. Acidify and test as usual.
  - Filtrate :—Yellow, chromate Cr. Confirm as usual.

To the solution of Group III precipitate in 6*N*-hydrochloric acid, which should be about 25 c.c. in volume, a saturated solution of sodium carbonate is added to turbidity. It is then cooled and a little sodium peroxide powder and 1-2 g. of sodium carbonate added and the mixture boiled slowly for about 10 minutes. It is diluted with 10 c.c. of water, and filtered by decantation ; the residue is treated again with a few c.c. of hydrochloric acid, neutralised and boiled with about 1 g. of sodium carbonate for 5 minutes and finally filtered and washed. The precipitate contains Fe, Bi, Mn, Ca and Mg as hydroxides or carbonates. (*Cf. note* 5).

Note 5. The treatment with sodium carbonate and sodium peroxide was found to convert practically completely the oxalates and phosphates of this group into carbonates,

Group IV.

Ppt.:—Oxides or phosphates of Ni, Co, Cu, Cd and Hg. Dissolve in 6*N*-hydrochloric acid and treat with Al and filter (*cf.* Note 6).

- Ppt:—Cu and Hg in metallic condition.
  - Test a small portion of ppt. with Cu foil for Hg.
  - Dissolve bulk of ppt. in nitric acid; boil off excess acid and test for Cu with potassium ferrocyanide in the usual way.
- Filtrate:—Treat with sodium hydroxide solution in excess, filter and wash.
  - Ppt.:—Cd, Co, Ni. Dissolve in acetic acid and treat with ammonium oxalate, filter and wash.
    - Ppt:—White Cd oxalate; dissolve in as little HCl as possible and add potassium ferricyanide, yellow ppt. Cd.
    - Filtrate:—Co, Ni. Concentrate and test, for Co with KNO_2 and for Ni, with dimethyl glyoxime in the usual way.
  - Filtrate:—Al. Reject

Group V.

Solution:—Zn and As.

Acidify with hydrochloric acid and boil with 3*N*-sodium carbonate solution and filter.

- Ppte.:—Zn CO_3. Dissolve in HCl and confirm by ferrocyanide test or Rinmann's green test with the Zn CO_3.
- Filtrate:—Sodium arsenate. Reduce with SO_2 and test for As by Bettendorf test.

Group VI.

(NH_4), K and Na.

The original mixture is treated with water containing a few c.c. of 6*N* HCl and filtered. A small portion of the filtrate is tested for (NH_4) by sodium hydroxide and the Na and K are tested for in the bulk of the solution, after removing other bases by Ba $(OH)_2$ and H_2SO_4 treatment, in the usual way.

Note 6. Treatment of the hydrochloric acid solution of Group IV ppt. with a small piece of Al foil precipitates all the Cu and Hg. Some nickel and cobalt may also be preipitated here. After the Al piece goes in solution, add about 5 c. c. of 6*N*-HCl and allow to stand a little when, precipitated Ni & Co, if any, would go in solution.

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CHEMICAL EXAMINATION OF *CLERODENDRON INFORTUNATUM*. PART I.

By Hirendra Nath Banerjee.

Clerodendron Infortunatum or the India *Bhant* or *Bhat* (N. O. *Verbenaceæ*) is a gregarious shrub, very common in the warm regions throughout India from Gurhwal and Assam to Ceylon. The importance of the plant from medicinal point of view has been advocated by Rheede, Dr. Bhola Nath Bose (Pharmacopoeia of India) and Thornton (*Pharmacographica Indica*, V., p. 79) as vermifuge, anthelmintic and also as a cheap and efficient substitute for *Chiretta*. In the indegenous system the young twigs of Bhant are ground into a thick paste and the pills prepared therefrom swallowed with water, for the destruction of intestinal worms.

In view of the facts mentioned above a systematic chemical investigation was undertaken to find out the active principles responsible for the therapeutic action of the drug and also as far as possible to elucidate their chemical constitution.

EXPERIMENTAL.

Test for Alkaloids.—50 G. of air-dried, finely powdered leaves when treated with Prollius fluid did not indicate the presence of any alkaloid.

Table I.

Analysis of leaf.

Ash ...	... 8·04%
Protein ...	21·12 (N, 3·33)
Crude fibre ...	... 14·84
Free reducing sugars ...	3·00
Total sugars after inversion ...	... 17·05

Table II.

Analysis of Leaf-ash.

Ash soluble in water	... 45·08%
Ash soluble in acid	... 47·57
Insolubles ..	... 7·35
SiO_2	... 7·35
MnO_2	... 0·116
Fe_2O_3	... 2·45
P_2O_5	... 2·82
CaO	... 24·70
MgO	... 10·28
Total alkali [$Na_2O + K_2O$]	... 32·28
Cl	... 2·20
SO_3	... 8·84
CO_2	... 8·40
Total determined ...	... 99·76%

Extraction with Various Solvents.—In order to ascertain the general character of the constituents present, 193 g. of air-dried leaf-powder were extracted successively in a Soxhlet apparatus with various solvents. The different extracts, thus obtained, were dried at 100° and weighed.

TABLE III.

Petroleum ether (b p. 30-50°) extract	3·85%
Ether extract	2·31
Chloroform extract	1·82
Absolute alcohol	8·75
Water extract	14·10
Residue left over	69·00
Loss by diff.	0·17
	100

Petroleum Ether Extract. Isolation of Clerodin.

The extract obtained from 3 kg. of air-dried leaf-powder consisted of a deep greenish yellow solution with an extremely bitter taste. On concentration, crystals appeared. These on recrystallisation from boiling 50% aqueous alcohol (charcoal) were obtained as colourless long glistening needles, extremely bitter in taste, m. p. 161°-62°.

The petroleum ether mother liquor was distilled off to remove the last traces of petroleum, when a deep green pasty mass was obtained. It was distilled in steam and the distillate was found to be turbid but free from any bitter taste. This distillate was found to contain a volatile essential oil with a strong odour of the drug. By repeated extraction with 60% alcohol a further crop of the bitter substance was obtained from the pasty mass. The total yield of the bitter substance amounted to 0·12% of the air-dried leaf.

Interesting physiological and chemical properties of the bitter substance, on which a note has been published (*Science and Culture*, 1936, 2, 163), will be the subject of a future communication. The substance has been named *clerodin*.

After complete removal of clerodin, the pasty mass was repeatedly extracted with 80% alcohol. The extract gave large silvery plates whic after recrystallisation from 80% alcohol (charcoal) appeared as hexago plates, m. p. 147°-48° answering to all the colour reactions of *sterols*, al getting precipitated by alcoholic digitonin. The *acetyl* derivative melted a 127°-28°. The yield of sterol was less than 0·01% of the Bhant leaf. Aft separation of the sterol the mother liquor deposits a substance in flakes in extremely small quantity, which seemed to be an alcohol, m. p. 75°.

The dark pasty residue was dissolved in ether and purified (charcoal and Fuller's earth). After removal of the solvent a dark-coloured butter-like mass was obtained. 12 G. of this substance were saponified and the crude fatty acids liberated and removed. The aqueous portion after treatment with barium carbonate and filtration was concentrated to a syrup under reduced pressure, and identified as glycerol by the acrolein test. The paste, therefore, contains a fixed oil. Determination of iodine value (76·1-75·7) and saponification value (186-176·1) shows that it contained much impurities, which could not be easily removed. 100 G. was, therefore, saponified with alcoholic potash, alcohol removed and the soap dissolved in water, when a rubber-like elastic cake (20 g.) separated out, and was removed. The soap solution was thoroughly washed with ether to remove all unsaponifiable matter, and the free fatty acids liberated and obtained in pure state.

TABLE IV.

Constants of the free fatty acid mixture.

Iodine-value (Hanus).	Neutralisation value.	Mean M. W.	Unsaponifiable matter.
111·42	183·9	305	4·75 %

The fatty acids were then separated into their solid and liquid components by the Twitchell process (*J. Ind. Eng. Chem.*, 1921, **13**, 806).

TABLE V.

	Yield	Iodine value.	Ref. index.	Neutralisation value.	Mean M. W.
Liquid acid ...	80 %	138·1	1·4840 at 30°	196	285·7
Solid acid ...	20	6·79	m. p. 70° s. p. 60°	170	329·4

Determination of the Individual Liquid Fatty Acids.—The liquid acid mixture obtained above was brominated at -10° in dry ether solution according to Eibner and Muggenthaler (Lewkowitsch, "Chemical Technology and Analysis of Oils, Fats, Waxes," Vol. I, p. 585).

Linolenic Acid.—After bromination, ether-insoluble hexabromide was precipitated, which was filtered, washed free from bromine, thoroughly dried and weighed. After recrystallisation from benzene the bromide melted at 177°-78°. (Found: Br, 63·66. Calc. for $C_{18}H_{30}O_2Br_6$: Br, 63·33 per cent).

The mother liquor from the ether-insoluble hexabromide was washed thoroughly with hypo and then with water. The ether was then distilled off and the residue redissolved in boiling petroleum ether and on cooling linolic tetrabromide did not separate.

Oleic Acid.—The petroleum ether solution was then evaporated when a brown oily mass consisting entirely of oleic dibromide was obtained. (Found: Br, 36·08. Calc. for $C_{18}H_{34}O_2Br_2$: Br, 36·18 per cent).

TABLE VI.

Composition of the liquid acid mixture.

	Yield.	Corresponding acid calculated.	Percentage of each acid in the mixture.
Oleic dibromide	2·50	1·60	74·88% Oleic
Linolenic hexabromide	1·47	0·54	25·13% Linolenic

Examination of the Solid Acids.—The solid acid mixture (15 g.) was converted into the methyl ester and fractionally distilled under reduced pressure (1 mm.). The saponification values of the different fractions were determined from which the mean M. W. were calculated. The respective acids were then liberated from their different fractions and their melting points determined.

TABLE VII.

Temp.	Wt.	Saponification value.	Mean M.W.	M. p. of liberated acid.	% of each in solid acid.
160—170°	1·62 g.	197·6	283·9	66-67°	
170—175°	2·18	194·8	287·9	66-68°	
175—180°	1·22	192·2	291·9	67-68°	Stearic acid% 48·82
180—190° rising up to 200°	4·83	174·0	321·9	75-77°	Lignoceric acid

Residue weighing 2·1 g was found to consist mainly of crude lignoceric acid.

Unsaponifiable Matter.

The unsaponifiable matter which was obtained as a non-crystalline mass with a waxy appearance and deep orange colour was preserved in a vacuum desiccator in a dark place. From this product after complete separation of all sterols, first by freezing out its methyl alcoholic solution, and then by precipitation with digitonin, the two pigments carotin and xanthophyll were separated by the method of Willstätter. These were identified by spectroscopic analysis as well as $SbCl_3$ reaction and Molisch's test.

Sterol.

The sterol portion obtained by freezing out the methyl alcoholic solution of the unsaponifiable matter after repeated crystallisation from alcohol with animal charcoal did not give a definite crystalline product with a sharp melting point. It melted at 138-140° with softening at 135° The acetate prepared direct from this product softens at 65° and melts at 68-70°. The whole of the sterol was, therefore, precipitated from solution by digitonin and the digitonide converted direct into the acetate. The sterol acetate, thus obtained, was a tuft of needles, m.p. 125-27°. The total amount of the sterol was, therefore, quantitatively estimated by the digitonin method of Windaus and the amount was found to be 1·20% of the oil.

The mother liquor left after separation of the sterol as digitonide was freed from any excess of digitonin and a quantity of waxy material with a characteristic odour was obtained. This dissolved completely in boiling acetic anhydride from which nothing separates on cooling. This evidently indicates that naturally occurring hydrocarbons are not present in any appreciable quantity but that aliphatic alcohols probably constitute the rest of the unsaponifiable matter.

The Ether Extract.—The ether extract of the leaf-powder after purification gave an oil which was found to be similar in composition to the oil obtained from the leaf by extraction with light petroleum ether. Saponification value, 184; iodine value, 76·23.

The viscous mass was found to contain traces of gallic acid, giving blue-black colouration with ferric chloride and a positive Young test for gallic acid (*Chem. News*, 1883, **48**, 31).

The Chloroform extract was not bitter and did not give any crystalline product. After extraction with 3% hydrochloric acid, the extract failed to give the usual test for the presence of alkaloids.

The Alcoholic extract on concentration and standing did not give any crystalline substance. After complete removal of the alcohol, the residue was dissolved in water. The opalescent solution, thus obtained, was thoroughly extracted with ether. From the ether solution gallic acid was obtained and identified by the preparation of triacetyl derivative, m. p 168-69°.

The aqueous solution after ether treatment was treated with lead acetate and then with lead subacetate. The filtrate freed from the precipitates was treated with sulphuretted hydrogen and the lead-free solution was concentrated to a syrup. The syrup reduced Fehling's solution and the amount of reduction did not show any increase after boiling with hydrochloric acid. The syrup was laevo-rotatory and the sugar content estimated polarimetrically agreed fairly well with that estimated by Benedict method and was 6·12% of the total alcoholic extract. Copious crystals of osazone were obtained, m.p. 202°-203°.

The Lead Acetate Precipitate was decomposed in aqueous suspension and the de-leaded material was found to consist of tannins only. Similarly the lead subacetate precipitate was found to contain tannin and a reducing sugar.

The Aqueous Extract.—The aqueous extract was thoroughly examined and found to consist of reducing sugars, traces of tannin, proteins, chlorides and sulphates.

TABLE VIII.

Amount of clerodin in different parts of the Bhant plant.

Young leaves & twigs collected before rains		0·12%
„ „	just after rains	0·55%
Old leaves		0·05%
Stem and roots		traces only.

Some Physiological Properties of Clerodin.

Effect of Clerodin on Red Blood Corpuscles.—Well washed R.B.C. suspended in physiological saline (2 c.c.) was added to 8 c.c. of saturated solution of clerodin (0·06%) in isotonic saline and thoroughly mixed together. The mixture was incubated at 37° for 24 hours, after which the R.B.C. was found to have completely settled down leaving a clear colourless solution above. Under the microscope the corpuscles were found to be intact showing that clerodin has no hæmolytic action on human R.B.C.

Bactericidal Action on B. Coli.—A 12 hours' culture of *B. Coli* in Neutrient broth (1 part) and clerodin solution (1 part) in sterile normal saline were thoroughly mixed and incubated for 24 hours at 37°. A subculture made from this mixture showed that *B. Coli* was not killed. Similar results were observed with different media, *e.g.*, peptone sloution, with lactose and glucose. Growth of *B.Coli* was evident by the production of acid and gas. Saturated aqueous solution of clerodin has no bactericidal property as tested against *B. Coli*, the most common member of the intestinal Flora.

Anthelmintic Property : Toxicity to Earthworms.—The toxicity of clerodin to earthworms was investigated according to the method of Sollman (*J. Pharm. and Exp. Therap.*, 1918, **12**, 129). The experience of Straub and Tradelenberg and also of Sollman indicates that in some cases the toxicity of drugs to earthworms may run more or less parallel with their toxicity to parasitic worms, although earthworms belong to a totally distinct zoological group. Drugs toxic to earthworms are considered to have possibilities as anthelmintics (Chopra and Chandler "Anthelmintic and their Uses," p. 20). In the present case clerodin has been found to kill earthworms in aqueous solution within 30 minutes.

Small fish *apolocheilus melastigma* were killed by such solution in half an hour and also mosquito larvæ in two hours, when experiments were carried out with them according to Fink and Haller (*J. Econ. Entom.*, 1936, **29**, 595). From all these experiments it will be evident that clerodin is toxic to lower order of life.

Clerodin is soluble in hydrochloric acid, olive oil, castor oil, glycerol, and slightly in liquid paraffin and vaselin. To see how far the drug may act injuriously to mammals, 0·1 g. of clerodin dissolved in 10 c.c. of olive oil was fed to a rabbit (body wt., 1·2 kg.). No injurious effect whatever was observed. Clerodin may, therefore, act as a vermifuge without any injurious effect on the host.

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A NOTE ON THE PREPARATION OF β-4-METHOXY-1-NAPTHOYLPROPIONIC ACID.

By K. P. Dave and K. S. Nargund.

A recent publication of Fieser and Hershberg (*J. Amer. Chem. Soc.*, 1936, **58**, 2314) renders it unnecessary to continue the work we have been doing since last July. The results already obtained are recorded below.

Ruzicka and Waldmann (*Helv. Chim. Acta*, 1932, **15**, 907) first obtained β-4-methoxy-1-naphthoylpropionic acid by condensing α-naphthol methyl ether with succinic anhydride in presence of aluminium chloride using carbon disulphide as the solvent. As the yields by this method were not good (30-40%) we investigated this reaction using different solvents and obtained 40% yield by the use of petroleum ether and 90-92% yield by using either nitrobenzene or acetylene tetrachloride as the solvents. β-4-Methoxy-1-napthoylpropionic acid has been characterised by the preparation of methyl ester (m.p. 56°) and an ethyl ester (b.p. 230°/15 mm.). The constitution of the acid has been further confirmed by its synthesis by the action of succinic anhydride on the Grignard reagent prepared from 4-bromo-1-methoxynaphthalene.

EXPERIMENTAL.

To a boiling suspension of succinic anhydride (4 g.) in benzene (20 c.c.) was added the Grignard reagent prepared from 4-bromo-1-methoxy-naphthalene (8 g.), magnesium (1.5 g.) ether (50 c.c.) and a crystal of iodine. It was warmed for half an hour on a water-bath, decomposed by ice and dilute sulphuric acid. The ether-benzene layer was once washed with water and then extracted with a dilute solution of sodium carbonate. On acidifying the sodium carbonate extract a greenish solid separated (2·5 g.), which on crystallisation from methyl alcohol melted at 172°. It did not depress the m.p. of β-4-methoxy-1-naphthoylpropionic acid.

Methyl β-4-methoxy-1-napthoylpropionate, prepared by esterifying the acid with methyl alcohol, is soluble in benzene, ethyl acetate and hot methyl alcohol, and melted at 56°. (Found: C, 68·28; H, 5·7. $C_{16}H_{16}O_4$ requires C, 68·43; H, 5·67 per cent).

Ethyl β-4-methoxy-1-napthoylpropionate had b.p. 230°/15 mm. (Found: C, 71·21; H, 6·29. $C_{17}H_{18}O_4$ requires C, 71·32; H, 6·29 per cent).

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ON THE PHOTOCHEMICAL OXIDATION OF ORGANIC SUBSTANCES BY HYDROGEN PEROXIDE IN ACID MEDIUM WITH INORGANIC SOLS AS PHOTOSENSITISER.

By Tarapada Banerjee.

In some unpublished papers from this laboratory, photochemical reactions have been studied with the following sols as photosensitisers :— Tungstic acid sol and ferric hydroxide sol As oxidants were used iodine, potassium indigo-tetrasulphonate and methylene blue.

These oxidants have generally absorption for radiations of 366 $\mu\mu$ and in determining the amount of effective intensity of radiation absorbed by the photosensitising sol alone, indirect methods of calculation had to be employed. The use of hydrogen peroxide as an oxidant removed this defect as it has comparatively small absorption at 366 $\mu\mu$. By carrying out experiments on photo-oxidation only in the range of p_H 1·5−4·8, the spontaneous decomposition of H_2O_2 was avoided. The use of hydrogen peroxide has also the advantage, that its concentration at any time during the progress of the reaction can be accurately estimated volumetrically.

It is well known that hydrogen peroxide reacts with tungstic acid, molybdic acid, vanadic acid and chromic acid sols to form pertungstates, permolybdates, pervanadates and perchromates.

Brode (*J. Phys. Chem.*, 1901, **37**, 299) observed that pertungstic acid remains fairly dissociated in solution. But quantitative data about the equilibrium constant was supplied by Pissarjewsky (*Z. physikal. Chem.*, 1903, **13**, 167), who deterimed the free H_2O_2 in aqueous solution by partition experiments with ether.

In experiment with 0·05*M*-Na_2WO_4 and 0·097*M*-H_2O_2 (in 0·125*M* H_2SO_4), the concentration as bound H_2O_2 was found by Pissarjewsky (*loc. cit.*) to be 0·0385%. So the concentrations of H_2O_2 and free tungstic acid sol are 0·0385*M* and 0·0115*M* respectively. Therefore the equilibrium constant

$$K = \frac{(0{\cdot}0585) \times (0{\cdot}0115)}{(0{\cdot}0385)} = 1{\cdot}75 \times 10^{-2}$$

With the help of this equilibrium constant, we can calculate the bound H_2O_2 in mixtures of different concentrations of H_2O_2 and tungstic acid sol. In Table I are given the concentrations of bound H_2O_2 when the concentration of tungstate is 0·025 *M* and that of H_2O_2 between 0·0112 *M* 0·0557 *M*, as was the case in our experiments on photocatalytic reaction with the system.

TABLE I.

Conc. of tungstate (*M*) ...	0·025	0·025	0·025	0·025	0·025	0·025
Conc. of H_2O_2 (*M*) ..	0·0112	0·017	0·0261	0·0353	0·038	0·0557
Conc. of bound H_2O_2 (*M*)...	0·00585	0·00830	0·01141	0·0138	0·01437	0·01719

It is evident from the above table that when the initial concentration of H_2O_2 is low, the concentration of bound H_2O_2 in the mixture is proportional to the initial concentration of H_2O_2, while at higher initial concentration of H_2O_2, the concentration of bound H_2O_2 remains practically unaffected by the change in the initial concentration of H_2O_2.

It is clear therefore that in a mixture containing a tungstate, hydrochloric acid and H_2O_2, we have free hydrogen peroxide, pertungstic acid and micelles of tungstic acid sol ; and it is very probable that the molecules of pertungstic acid is adsorbed on the surface of these micelles. The process of photocatalysis may be depicted as follows :—

Activated pertungstic acid on micelle surface + reduction
= tungstic acid sol + oxidised product.

Tungstic acid + H_2O_2 = pertungstic acid.

The mechanism of photo-oxidation is similar in the case of other sols, but quantitative data on the equilibrium between the acid sol, peracid and hyrogen peroxide are not available.

Permolybdates have been described by Pechard, Pissarjewsky and others. Owing to dissociation and *formation of colloidal complexes*, the results are not reliable. The general results therefore show that there are two permolybdic acids, permonomolybdic acid (MoO_3, H_2O_2 and H_2MoO_5) and perdimolybdic acid ($MoO_3,2H_2O_2$ or H_4MoO_6).

Pervanadic Acid.—Meyer and co-workers (*Z. anal. Chem.*, 1926, **69**, 1520) found that V_2O_5 dissolves in H_2O_2 giving a pale yellow solution, which appears to contain vanadic acid *in a colloidal form* ; at the same time H_2O_2 is catalytically decomposed.

Vanadic Acid Sol.—We have found that in presence of sufficient acetic acid, the vanadic acid sol prepared by the action of acetic acid on sodium vanadate does not decompose hydrogen peroxide and is not coagulated during the process of oxidation of glucose.

According to Canneri (*Gazzetta*, 1926, **56**, 11,779), the electrical conductivity of solutions of sodium metavanadate acidified with increasing quantities of acetic acid varies continuously at 30°, indicating that condensation of molecules of metavanadate is a continuous function of the concentration of acetic acid.

Dumanski in a series of papers has established the point of view that with progressive increase in the number of atoms of vanadium in a molecule of vanadic acid, the colloid-chemical properties become more and more manifest.

Perchromic Acid.—When hydrogen peroxide is added to chromic hydroxide, per-compounds are formed (Barreswil, *Ann. chim. phys.*, 1848, *iii*, **20**, 364). When the concentration of hydrogen peroxide and chromic acid is very high, the per-salt decomposes liberating oxygen. But in very dilute solutions, when the concentration of hydrogen peroxide is less than that of chromic acid, we found that the per-salt is stable and no decomposition was observed for 8 hours in a quartz vessel (*vide* Section F).

Experimental Arrangement.—The source of light was a point source quartz mercury lamp which was run from a battery of 30 volts. An ammeter in circuit and a variable external resistance were used to keep the strength of current at values between 2 and 2·6 amperes.

For isolating monochromatic radiations at $366\mu\mu$, Schott and Gen ultraviolet filter No. 312 was used. In the case of red light, a thousand c.p. point-o-lite Ediswan Lamp was used with suitable filters. Wave-length $579\mu\mu$ was isolated with the help of Zeiss monochromators.

Light from the lamp was rendered parallel by a quartz lens placed at its focal distance from the lamp and passed into the reaction vessel, kept inside a double jacketed box through a window of fused quartz plate. The temperature was kept constant within 0·1° by circulating water from a thermostat through the annular space of the box. The reaction vessel was a rectangular stoppered cell made of plane parallel plates of fused transparent silica.

No cement was used, the rectangular joints being fused to one another. The closed stopper was very well ground into a circular aperture in the thick top plate of the reaction cell.

The intensity of incident radiation was varied by using quartz lenses of different focal lengths. The method of measuring intensities actually absorbed by the reaction mixture consisted in first observing the deflection in a Moll galvanometer with a Moll surface thermopile, covered with a quartz window and placed immediately behind the reaction cell which contained only water. The deflection was next noted when the cell was filled with the reaction mixture. The difference gave the quantity of radiant energy absorbed by the reacting system. The thermopile recording system was frequently calibrated by means of a Standard incandescent lamp, tested by the National Bureau of Standards, Washington. The scattering power for light was found very small in the case of the sols (unpublished work by Ghosh and Banerjee).

In experiments with hydrogen peroxide, cleanliness must be scrupulously observed, it being very unstable in presence of dust particles. In these experiments most of the apparatus, including the Pyrex titrating vessels, were steamed one day before the time for carrying out an experiment and kept in a glass case. All the apparatus were not allowed to come in contact with any solid substance except glass. One glass hooked pipette stand was made for the purpose.

All extra-pure chemicals (Merck or Kahlbaum) were used in these experiments. Hydrogen peroxide used was Merck's Reagent 'Perhydrol' stocked in paraffined bottle. The rate of reaction was followed by estimating the decrease in the concentration of hydrogen peroxide with time. For estimating hydrogen peroxide, the well known standard method of Kingzett (*J. Chem. Soc.*, 1880, 792) was adopted. 0·2—0·3 C.c. of reaction mixture was taken for each titration with a micropipette. The iodine liberated was estimated with standard thiosulphate (generally 0·01*N*) from a microburette, reading direct to 0·01 c.c., using freshly prepared starch solution as internal indicator. On performing the blank experiments with redistilled water, sulphuric acid and potassium iodide at 80° the temperature at which the estimation was carried, it was seen that iodine liberated in 15 minutes is practically nil. It must be mentioned here that throughout these series of experiments, redistilled water was used for preparing all the solutions. The hydrogen peroxide was freshly prepared before each day's experiment as it decomposes in glass vessel after standing for some time (about 10-12 hours). It is stable in quartz vessel for a much longer time. For measuring temperature coefficient, maximum temperature used was 37°·5, as above this temperature, hydrogen peroxide becomes unstable and gives erratic results.

A. The Photochemical Oxidation of Glucose by Hydrogen Peroxide in Acid Medium with Tungstic Acid Sol as Photosensitiser.

In presence of light, hydrogen peroxide cannot oxidise glucose in acid solution but when some photosensitiser, *e.g.*, tungstic acid sol is added to the system, oxidation commences.

A mixture of glucose, hydrogen peroxide, hydrochloric acid, and sodium tungstate does not react when kept in the dark for a sufficiently long time (14 hours).

The unimolecular velocity constant was calculated by the formula $K = 2{\cdot}3 \times 1/t \log (a/a-x)$ where t is reckoned in seconds. The zero-molecular velocity constant K_0 is given by the number of g. mols. transformed in 1 second in a unit cell (1 cm. × 1 cm. × 1 cm.).

TABLE II*a*.

Effect of varying the concentration of hydrogen peroxide.

Wave-length = 366$\mu\mu$. Temp. of thermostat = 32°·5. Strength of thiosulphate = 0·01N. H_2O_2 = 0·017M. Conc. of sodium tungstate = 0·025M. Conc. of HCl = 0·0783N. Conc. of glucose = 0·025M. Intensity of absorbed radiation = 2030 ergs per sq. cm. per sec.

Time.	Pertungstate.	C c. thiosulphate ≡0·232 c c. reaction mixture	K_{unimol} with respect to H_2O_2 $= 2{\cdot}3 \times 1/t_{\text{sec}} \log a/a-x$.
0 min.		0·755	
60	0·0071M	0·655	5·36 × 10^{-5} (Induction period)
120	0·0054	0·475	8·92 × 10^{-5} (between 283)
180	0·0040	0·345	8·90 × 10^{-5} (between 284)
		Mean	8·92 × 10^{-5}

TABLE II*b*.

Conc. of hydrogen peroxide = 0·0353M. Other factors same as before.

Time.	Pertungstate.	C c. thiosulphate ≡0·232 c c. reaction mixture.	K_0 (zeromolecular with respect to H_2O_2, expressed in g mols. transformed per sec. in a unit cell).
0 min.		1·64	
60	0·0133M	1·54	
120	0·0122	1·35	12·0 × 10^{-10}
182	0·011	1·16	11·8 × 10^{-10}
		Mean	11·9 × 10^{-10}

TABLE III.

Tungstate = 0·025*M*. Glucose = 0·025*M*. Intensity of absorbed radiation = 2030 ergs per sq. cm. per sec. Thiosulphate = 0·01*N*. *d* (thickness of reaction cell) = 1 cm. Conc. of HCl added = 0·0783*N*.

H_2O_2.	Per-tungstate.	$K_{unimol} \times 10^5$	$K_0 \times 10^{10}$.	γ (quantum efficiency).
0·0112*M*	0·00585*M*	9·04		1·40
0·017	0·00830	8·92		1·50
0·0353	0·0138		11·90	1·92
0·038	0·01437		11·90	1·92
0·0557	0·01719		12·41	1·97

TABLE IV.

Sodium tungstate = 0·025*M*. HCl added = 0·0766*N*. Intensity of absorbed radiation same as in Table II.

Glucose.	H_2O_2.	Per-tungstate.	$K_{unimol} \times 10^5$.	$K_0 \times 10^{10}$.
0·0063*M*	0·0174*M*	0·00845*M*	8·44	
,,	0·034	0·0135		12·02
0·05	0·0172	0·00835	9·13	
,,	0·0373	0·0142		12·63

It will be noticed from Tables II and III that the reaction follows the unimolecular law when the concentration of hydrogen peroxide is low, but at very high concentration of hydrogen peroxide the reaction is zeromolecular. In this respect, it resembles the heterogeneous gaseous reactions. The concentration of hydrogen peroxide is without any appreciable influence on the unimolecular or the zeromolecular velocity constants.

There is a considerable period of induction at the beginning of the reaction and this increases with the increase in the concentration of hydrogen peroxide.

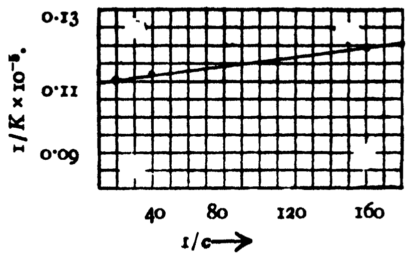
TABLE V.

Effect of varying the concentration of glucose.

Intensity of absorbed radiation per sq. cm. per sec. = 2030 ergs.

Glucose.	H_2O_2.	HCl added.	Conc. of tungstate.	$K_{unimol} \times 10^5$.
0·05 *M*	0·0172 *M*	0·0766 *N*	0·025 *M*	9·13
0·025	0·017	,,	,,	8·92
0·0063	0·0174	,,	,,	8·44

FIG. 1.



Though $1/c$ plotted against $1/K$ gives us approximately a straight line (Fig. 1), the variation in K with concentration of glucose is so small that the velocity constant may be taken as practically independent of the concentration of glucose.

Effect of Varying the p_H of the Reacting System.—The p_H of the system was kept constant with citrate buffer. It was found that citrate buffer did not react with hydrogen peroxide in presence of sol even in the ultraviolet light. It must be mentioned here that citrate buffer was found to inhibit the spontaneous decomposition of hydrogen peroxide even when the concentration of hydrochloric acid in the reaction mixture was very low. The hydrogen ion concentration of the reaction mixture was determined electrometrically using a quinhydrone electrode.

TABLE VI.

Sodium tungstate = 0·025*M*. H_2O_2 = 0·017*M*. Glucose = 0·025*M*.
Thiosulphate = 0·01*N*.

HCl added.	p_H of reaction mixture.	Energy absorbed in ergs/sq.cm./sec.	$K_{unimol} \times 10^5$.
0·0318 *N*	4·78	1843	2·37
0·0366	3·07	2500	9·36
0·0414	2·39	2580	10·07
0·0462	2·11	2580	7·89
0·0510	1·94	2580	7·41
0·0558	1·83	2580	6·90

The velocity of reaction at first increases rapidly with the decrease in the p_H value of the reacting system, reaches a maximum value and then decreases with the further decrease in the p_H value of the system. The reaction is minimum when the concentration of HCl added is nearly 1·5 times the concentration of sodium tungstate.

TABLE VII.

Effect of varying the intensity of absorbed radiation.

d (thickness of the reaction cell) = 1 cm. Glucose = 0·025M.
Tungstate = 0·025M.

* I_{abs}	HCl added.	H_2O_2.	$K_{unimol} \times 10^5$.	$K_0 \times 10^{10}$.
(a) 2030	0·0783 N	0·038 N	—	11·91
919	0·0766	0·0384	—	8·27
(b) 2030	0·0783	0·017	8·92	—
919	0·0766	0·0172	6·02	—

The velocity constants vary as the square root of the absorbed radiation.

Temperature Coefficient.—The temperature coefficient is small, being of the order of 1·1 – 1·2.

Quantum Efficiency of the Process.—The calculation of two typical examples are given below. The dimension of quartz cell in this case was 1·8 cm. × 1·8 cm. × 1 cm.

Example 1. Here the velocity constant is unimolecular.

In Table II*a*, the intensity of absorbed radiation per sq. cm. per sec. by a column of solution 1 cm. thick

$$= 2030 \text{ ergs} = \frac{2030 \times 3{\cdot}66 \times 10^{-7}}{(6{\cdot}55 \times 10^{-27}) \times (3 \times 10^{10}) \times (6{\cdot}1 \times 10^{23})} \text{ Einstein}$$

$$= 6{\cdot}20 \times 10^{-10} \text{ Einstein.}$$

Again the number of g. mols. transformed in unit time in a unit cell (1 cm. × 1 cm. × 1 cm.) (taking readings for 120 minutes after the induction period was over)

$$= \frac{\frac{0{\cdot}31}{0{\cdot}232} \times 0{\cdot}01}{2 \times 1000 \times 120 \times 60} = 9{\cdot}87 \times 10^{-10}.$$

Quantum efficiency of the process

$$= \frac{\text{No. of g. mols. transformed}}{\text{No. of Einsteins absorbed}} = \frac{2{\cdot}87 \times 10^{-10}}{6{\cdot}2 \times 10^{-10}} = 1{\cdot}59.$$

---

* In this and other tables that follow, $I_{abs.}$ signifies intensity of absorbed radiation in ergs/sq. cm./sec.

Example 2. Here the velocity constant is zeromolecular (Table II*b*).

Intensity of absorbed radiation $=6{\cdot}2\times10^{-10}$ Einstein (as before). No. of g. mols. transformed in 1 sec. in a unit cell

$$=K_0=\frac{11{\cdot}91\times10^{-10}}{1}.$$

$$\text{Quantum efficiency}=\frac{11{\cdot}91\times10^{-10}}{6{\cdot}2\times10^{-10}}=1{\cdot}92.$$

The mechanism of reaction in the present case, when tungstic acid sol acts only as photocatalyst with H_2O_2 as oxidant and glucose as reductant, is materially different from that of the photo-reaction when tungstic acid sol itself was the active oxidising agent. There the reaction was always zeromolecular and the velocity of reaction was proportional to the intensity of radiation absorbed.

In this case, however, the following characteristic features are observed :—

(1) For relatively high concentration of H_2O_2, the reaction is zeromolecular with respect to H_2O_2 but for lower concentration of H_2O_2 it is unimolecular.

(2) The velocity of reaction is proportional to the square root of the intensity of absorbed radiation.

(3) The quantum efficiency is generally greater than unity calculated on the assumption that the whole of the absorbed radiation is available for photo-activation.

(4) The inverse of the velocity constant plotted against the inverse of the concentration of the reductant is a straight line.

The following mechanism explains all these characteristics.

The whole of the absorbed radiation is assumed to be effective for purposes of photochemical transformation.

A quantum of absorbed radiation decomposes a molecule of pertungstic acid thus :—

PT (adsorbed on tungstic acid sol) + $h\nu$ $\longrightarrow$ T + O ... ... (1)
$[WO_2]\,(OH)\,[O_2H]=O+WO_2(OH)_2$ ... ... (1)
O + PT (adsorbed on tungstic acid micelle) $\longrightarrow$ O_2(active) + T ... (2)
O_2 (active) $\longrightarrow$ O_2 (normal) ... ... (3)
O_2 (active) + glucose $\longrightarrow$ gluconic acid + O ... ... (4)
O + O $\longrightarrow$ O_2 ... ... (5)

The stationary concentration of O atom is given by

$$\frac{I}{h\nu} = K_5[O]^2 + K_4[O_2 \text{ active}]\ C^s_a + K_2[O]\ C_{s[PT]}$$

where $C_{s[PT]}$ is the surface concentration of pertungstate and C_a is the surface concentration of glucose.

Reactions (4) and (2) have practically the same velocity.

Hence, $$[O] = \sqrt{\frac{I}{K_5 h\nu}}\,.$$

The stationary concentration of O_2 active is given by

$$K_2[O]C_{s[PT]} = K_3[O_2 \text{ active}] + K_4[O_2 \text{ active}]\ C^s_a$$

or $$[O_2] \text{ (active)} = \frac{K_2\left[\dfrac{I}{K_5 h\nu}\right]^{\frac{1}{2}} C_{s[PT]}}{K_3 + K_4\ C^s_a}$$

Hence the velocity of oxidation of glucose is given by (4)

and is $$= \sqrt{\frac{I}{K_5 h\nu}}\,.\,K_2 C_{s[PT]}\,.\,\frac{K_4\ C^s_a}{K_3 + K_4\ C^s_a}$$

$$= \sqrt{\frac{I}{K_5 h\nu}}\,.\,K_2\,.\,\frac{K' C_{PT\ (\text{Bulk})}}{K'' + K' C_{PT\ (\text{Bulk})}}\,.\,\frac{K_4\ C^s_a}{K_3 + K_4\ C_a}\,.$$

It is probable that the absorptive capacity of tungstic acid micelles for pertungstic acid molecules will be very large, so that practically all the latter molecules may exist in the surface phase. Even then, it would be expected, as already pointed out, that the concentration of pertungstic acid will be proportional to the concentration of H_2O_2 at low concentrations of the latter; hence in this region we should observe unimolecular velocity constants; but when concentration of H_2O_2 is large, $C_{PT\,(Bulk)}$ remains practically constant and we get zeromolecular velocity constants.

Again according to Langmuir,

$$C_G = \frac{K_6\, C_B^R}{K_7 + K_6 C_B^R}$$

where C_B^R is the bulk concentration of the reductant.

When C_B^R is very large, $K_7 + K_6\, C_B^R$ may be taken practically equal to $K_6\, C_B^R$, and we have dx/dt practically independent of C_B^R under otherwise identical conditions, as has been experimentally found to be the case.

B. Induction Period.

The photochemical oxidation of glucose by hydrogen peroxide in acid medium with ordinary tungstic acid sol as photosensitiser is attended with a large period of induction. Some typical data are shown in Table VIII.

TABLE VIII.

I_{abs}.	Glucose.	HCl.	H_2O_2.	Tungstate.	Period of induction.
(a) 2030	0·025*M*	0·0783*N*	0·038*M*	0·025*M*	29 min.
919	,,	0·0766	0·0384	,,	53
(b) 2030	,,	0·0783	0·020	,,	25
919	,,	0·0766	,,	,,	41

∴ Period of induction increases as the intensity of absorbed radiation decreases.

The influence of various variables, *e.g.*, concentration of reactants, intensity of radiation, etc., on the period of induction was studied and the observations may be summarised thus:—

(*i*) The induction period suddenly becomes very great when the molar conc. of hydrogen peroxide exceeds the concentration of sodium tungstate.

(*ii*) The induction period increases as the p_H of the system decreases.

(*iii*) The induction period decreases as the intensity of absorbed radiation increases.

Photo-reaction with Pre-excited Tungstic Acid Sol.—Here tungstic acid sol was first exposed to ultraviolet light for a sufficiently long time (about 3 hours) and then mixed with other components of the reacting system. The results are given below.

TABLE IX.

(*a*) Glucose $= 0{\cdot}025M$. HCl $= 0{\cdot}08N$. $H_2O_2 = 0{\cdot}0158$. Sodium tungstate $= 0{\cdot}025M$. Temp. $= 32°{\cdot}5$. Thiosulphate $= 0{\cdot}01N$. $d = 0{\cdot}5$ cm.

Intensity of absorbed radiation = 461 ergs per sq. cm. per sec.

Time.	C.c. thiosulphate ≡ 0·232 c.c. reaction mixture.	$K_{unimol} \times 10^5$.
0 min	0·73	...
58	0·625	4·44
118	0·54	4·26
	Mean	4·37

(*b*) $H_2O_2 = {\cdot}029N$. $d = 0{\cdot}5$ cm. Other factors same as in (*a*).

Time.	C.c. thiosulphate ≡ 0·232 c.c. reaction mixture.	$K_0 \times 10^{10}$ (No. of g. mols. transformed in 1 sec. in a unit cell).
0 min.	1·34	...
57	1·20	8·80
130	1·02	8·84
	Mean	8·82

The induction period observed before disappeared when the sol was matured by exposure to the effective radiation before it is mixed with the other components of the reacting system. Here again the velocity constant is unimolecular when the concentration of H_2O_2 is low and at higher concentration of hydrogen peroxide it is zeromolecular. The concentration of hydrogen peroxide is without any appreciable influence on the unimolecular or the zeromolecular velocity constants, and under similar conditions of experiment the velocities observed are nearly the same as in Section A.

TABLE X.

Effect of varying the concentration of hydrogen peroxide

Intensity of absorbed radiation = 950 ergs per sq. cm./per sec. d = 0·5 cm. Sodium tungstate = 0·025M. HCl added = 0·08N.

Glucose (M)	0·0125	0·0125	0·0125	0·0125	0·0125	0·025	0·025	0·025	0·0063	0·0063
H_2O_2.	0·011	0·014	0·0157	0·0284	0·0343	0·0118	0·015	0·028	0·0112	0·029
$K_{unimol} \times 10^5$	6·56	6·21	6·51			6·51	6·56		6·26	
$K_0 \times 10^{10}$				12·56	12·61			12·52		12·40

TABLE XI.

Effect of varying the concentration of glucose.

Glucose.	Tungstate.	H_2O_2.	HCl.	$K_{unimol} \times 10^5$.
0·025M	0·025M	0·011M	0·08N	6·56
0·0125	,,	0·0118	,,	6·51
0·0063	,,	0·0112	,,	6·26

The velocity constant is practically independent of the concentration of glucose.

TABLE XII.

Variation of the intensity of absorbed radiation.

I_{abs}.	Glucose.	Tungstate.	H_2O_2.	HCl.	$K_{unimol} \times 10^5$.	$K_0 \times 10^{10}$.
(a) 950	0·025M	0·025M	0·0157M	0·08N	6·51	
461	,,	,,	0·0159	,,	4·18	
(b) 950	,,	,,	0·0284	,,		12·56
461	,,	,,	0·0288	,,		8·84

The velocity constants vary as the square root of absorbed radiation.

Effect of Varying the p_H of the System.—The p_H of the system was kept constant with citrate buffer as in the previous section. No reaction was found between citrate buffer and hydrogen peroxide in presence of pre-excited tungstic acid sol in the ultraviolet.

TABLE XIII.

Glucose	Tungstate	H_2O_2.	p_H.	$K_{unimol} \times 10^5$
0·025*M*	0·025*M*	0·0180*M*	6·39	1·20
,,	,,	0·0180	5·41	2·35
,,	,,	0·0145	4·41	7·82
,,	,,	0·0140	1·17	7·36
,,	,,	0·0145	1·13	6·44

The mechanism of reaction is the same as that with unpre-excited tungstic acid sol.

C. *Photo-oxidation of Formaldehyde and Lævulose.*

The reaction is more or less similar to the oxidation of glucose by hydrogen peroxide in acid medium with tungstic acid sol as photo-catalyst with some exceptions. Neither of these reactions had any induction period. There is no dark reaction in both the cases. The velocity of reaction obeyed unimolecular law for low concentrations of hydrogen peroxide. The influence of the nature of polarisation of the exciting light was studied. Formaldehyde was standardised by estimating with iodine and sodium thiosulphate (*vide* Plimmer, "Practical Organic and Bio-chemistry" p. 85). Pfanstiel's lævulose was used for the reaction.

TABLE XIV.

(*a*) $H_2O_2 = 0{\cdot}02M$. Tungstate $= 0{\cdot}025M$. HCl $= 0{\cdot}0877N$. Formaldehyde $= 0{\cdot}0362\ M$. Thiosulphate $= 0{\cdot}01N$. Temp. $= 22°$. $I_{abs} = 1930{\cdot}6$ ergs.

Time.	C.c. thiosulphate = 0·3 c.c. of the reaction mixture.	K_{unimol} with respect to H_2O_2.	K_{mean}.	Quantum efficiency.
0 min.	1·42	—		
60	1·29	$2{\cdot}85 \times 10^{-5}$		
120	1·16	$2{\cdot}92 \times 10^{-5}$	$2{\cdot}85 \times 10^{-5}$	1·02
210	1·00	$2{\cdot}76 \times 10^{-5}$		

(*b*) $H_2O_2 = 0{\cdot}02M$. Tungstate $= 0{\cdot}025M$. HCl $= 0{\cdot}078N$. Lævulose $= 0{\cdot}025\,M$. Thiosulphate $= 0{\cdot}01N$. Temp. $= 22°$. $I_{abs.} = 1931$ ergs.

Time.	C.c. thiosulphate = 0·3 c.c. of the reaction mixture.	K_{unimol} with respect to H_2O_2.	K_{mean}.	Quantum efficiency.
0 min.	1·190			
60	0·925	$7{\cdot}02 \times 10^{-5}$	$6{\cdot}97 \times 10^{-5}$	2·05
140	0·660	$7{\cdot}02 \times 10^{-5}$		
240	0·440	$6{\cdot}90 \times 10^{-5}$		

From the above table it is quite evident that neither of the reactions has any period of induction.

TABLE XV.

Effect of varying the intensity of absorbed radiation.

$\lambda = 366\mu\mu$. Temp. $= 22°$. Conc. of tungstate $= 0{\cdot}25M$. Conc. of $H_2O_2 = 0{\cdot}02M$.

	I_{abs}.	Reductants.	HCl added.	$K_{unimol} \times 10^5$.
(a)	1931 ergs	H CHO (0·036*M*)	0·0877*N*	2·85
	668	„ „	„	1·17
(b)	1931	Lævulose (0·025*M*)	0·078*N*	6·97
	772	„ „	„	4·03

The velocity constant under otherwise similar conditions varies as the square root of the intensity of radiation absorbed.

The mechanism of reaction is the same as with glucose as the reductant.

D. Influence of Promoters.

No photochemical oxidation of glucose in presence of a promoter only, in absence of tungstic acid sol, was observed. Sol, pre-activated for 3 hours was used in each experiment and thereby the induction period was avoided. The results are given below.

TABLE XVI.

$\lambda = 366\mu\mu$. Temp. of thermostat $= 31^\circ$. Glucose $= 0{\cdot}025M$. Tungstate $= 0{\cdot}025M$.

Promoter used.	Conc. of promoter.	$I_{abs.}$	H_2O_2.	Conc. of acid added.	Constant with promoter.	Constant without promoter under otherwise identical conditions.
$FeCl_3.6H_2O$	$M/10{,}000$	696 ergs.	$0{\cdot}034M$	$0{\cdot}08N$	$19{\cdot}64 \times 10^{-10}$ (zeromol)	$10{\cdot}91 \times 10^{-10}$ (zeromol)
,,	,,	,,	0·0287	,,	$13{\cdot}81 \times 10^{-10}$ (zero)	$10{\cdot}91 \times 10^{-10}$ (zero)
,,	,,	,,	0·0136	,,	$5{\cdot}59 \times 10^{-5}$ (uni)	$3{\cdot}96 \times 10^{-5}$ (uni)
,,	,,	,,	0·0110	,,	$5{\cdot}75 \times 10^{-5}$ (uni)	$3{\cdot}96 \times 10^{-5}$ (uni)
,,	$M/5000$	1513	0.0348	$0{\cdot}1175N$	$22{\cdot}18 \times 10^{-10}$ (zero)	$14{\cdot}68 \times 10^{-10}$ (zero)
,,	,,	,,	0·0286	,,	$17{\cdot}36 \times 10^{-10}$ (zero)	$14{\cdot}68 \times 10^{-10}$ (zero)
,,	,,	,,	0·0146	,,	$8{\cdot}58 \times 10^{-5}$ (uni)	$7{\cdot}43 \times 10^{-5}$ (uni)
,,	,,	,,	0·0091	,,	$10{\cdot}99 \times 10^{-5}$ (uni)	$7{\cdot}43 \times 10^{-5}$ (uni)
$FeSO_4, 7H_2O$	$M/20{,}000$	2980	0·0123	,,	$15{\cdot}34 \times 10^{-5}$ (uni)	$10{\cdot}97 \times 10^{-5}$ (uni)
$CuSO_4,6H_2O$	,,	,,	0·0131	,,	$15{\cdot}76 \times 10^{-5}$ (uni)	$10{\cdot}97 \times 10^{-5}$ (uni)
Manganese citrate	,,	,,	0·131	,,	$14{\cdot}42 \times 10^{-5}$ (uni)	$10{\cdot}97 \times 10^{-5}$ (uni)

As in the experiments without a promoter, here also the veocity of reaction obeys the unimolecular law when the concentration of hydrogen peroxide is low and is zeromolecular when the concentration of hydrogen peroxide is high.

The general mechanism of promoter action is not known with certainty. The promoter may (*i*) increase the number of active points on the catalyst surface,—the area of the surface round about the promoter atom being more reactive ; (*ii*) may prevent the destruction of the active point during the course of reaction ; (*iii*) may retard the transformation of active intermediate reactants into normal inactive forms.

In the photochemical reactions which we have studied, the reaction is initiated by the absorption of a quantum of radiation and hence hypotheses (*i*) and (*ii*) about regarding promoter actions are not applicable.

The promoters somehow retard reaction (3) in conversion of O_2 (active) into O_2 (normal) or reaction (5), *i. e.*, conversion of two oxygen atoms into a molecule of oxygen (*vide* Section A, discussion).

Yoshimera (*J. Soc. Chem. Ind. Japan*, 1934, **37**, 350) explained the promoter action of Cr_2O_3 in $Fe_2O_3—Cr_2O_3$ catalyst in the production of hydrogen by means of water gas reaction by assuming that Cr_2O_3 retards the movements of active atoms to inactive positions.

E. *Chromic Tungstate as Photosensitiser.*

Tungstic acid sol absorbs only ultraviolet light whereas chromic tungstate sol, in addition to general absorption in the ultraviolet, has absorption bands in the yellow and the red. The present investigation was undertaken to study the above photo-oxidation in details in light of different wave-lengths.

Preparation of Chromic Tungstate Sol.—The sol was prepared after Dhar and Prakash (*J. Indian Chem. Soc.*, 1930, 7, 367).

Estimation of Tungstic Acid in Chromic Tungstate Sol.—Tungstic acid in chromic tungstate was estimated by precipitating the tungstic acid with the help of hydrochloric acid and cinchonine hydrochloride (*cf.* Treadwell and Hall, " Analytical Chemistry ", 1924, Vol. II, p. 268) and igniting the precipitate as WO_3.

In this paper the molar concentration of chromic tungstate is expressed in terms of WO_3.

For red light, a point-o-lite lamp of 1000 c. p. run at a constant current of 5 amperes was used.

TABLE XVII.

Effect of varying the concentration of hydrogen peroxide.

Region = 750 – 600 $\mu\mu$. d = 1 cm. Glucose = 0·025*M*. HCl = ·0562*N*.

$I_{abs.}$	H_2O_2.	Chromic tungstate.	K_0 (No. of g. mol. transformed per sec in a unit cell) (P).	$\frac{P}{Q} \times 10^{12}$.	Quantum efficiency.
4500 ergs.	0·0173*M*	0·02052*M*	13·79 × 10^{-10}	3·06	0·54
,,	0·0182	,,	13·49 × 10^{-10}	3.00	0·53
,,	0·0183	,,	13·79 × 10^{-10}	3·06	0·54
,,	0·0235	,,	13·19 × 10^{-10}	2·91	0·52
,,	0·0252	,,	13·49 × 10^{-10}	3·00	0·53
3500 ergs.	0·0099	0·01231*M*	10·49 × 10^{-10}	3·00	0·53
,,	0·0128	,,	10·79 × 10^{-10}	3·08	0·54
,,	0·0175	,,	10·40 × 10^{-10}	2·97	0·57
,,	0·0183	,,	10·49 × 10^{-10}	3·00	0·53
,,	0·0212	,,	10·79 × 10^{-10}	3·08	0·54

TABLE XVIII.

Region $=366\mu\mu$. $I_{abs.}=2030$ ergs $=6·2\times10^{-10}$ Einstein. Glucose $=0·025M$. HCl $=·039N$. Chromic tungstate $=0·0082N$.

H_2O_2.	$K_{unimol}\times10^5$.	$K_0\times10^{10}$.	Quantum efficiency.
0·0121 M	5·01	...	0·9
0·023	5·01	...	1·7
0·0374	...	5·04	0·815
0·0463	...	4·92	0·80
0·0489	...	4·92	0·80
0·0560	...	5·01	0·81
0·0740	...	5·04	0·815

From Table VIII it will be seen that in the region $750-600\mu\mu$, the reaction always obeys the zeromolecular law but when the region $(366\mu\mu)$ is used as the exciting radiation (Table VIII), the reaction is monomolecular at low concentrations of hydrogen peroxide but at high concentrations of hydrogen peroxide, the reaction is zeromolecular (*cf.* Tables XVII and XVIII).

In the region $750-600\mu\mu$, the velocity constant is proportional to the intensity of absorbed radiation (*vide* Table XVII, P/Q).

The reaction is always attended with a very large period of induction.

TABLE XIX.

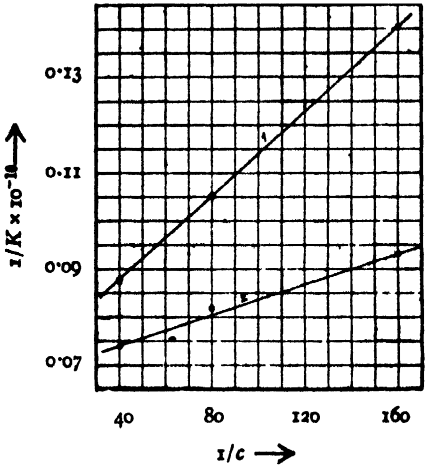
Effect of varying the concentration of glucose.

Region used $=750-600\mu\mu$. HCl $=0·0562N$.

Glucose.	H_2O_2.	Tungstate.	$I_{abs.}$	$K_0\times10^{10}$.
0.025M	0·0152M	0·02052M	4500 ergs	13·49
0·0125	0·0153M	,,	,,	11·99
0·00625	,,	,,	,,	10·79
0·025	0·01M	0·01231M	3500	11·40
0·0125	,,	,,	,,	9·59
0·00625	,,	,,	,,	7·19

$1/c_{(\text{glucose})}$ plotted against $1/K$ gives approximately a straight line (Fig. 2).

FIG. 2.



Curves 1 and 2 refer respectively to 0·01231M sol and 0·0205M sol.

TABLE XX.

Effect of varying the concentration of hydrochloric acid.

Region = 750 − 600μμ. H_2O_2 = 0·00927M. Chromic tungstate = 0·02052M.

Glucose.	HCl.	I_{abs}.	$K_0 \times 10^{10}$.
0·025M	0·0562N	4500 ergs	13·79
,,	0.0390N	,,	14·99
,,	0·0260N	,,	15·59

The velocity constant increases as the concentration of free hydrochloric acid diminishes. It is well known that hydrogen peroxide becomes more stable, the more acid is added to its solution.

Effect of varying the temperature.—The temperature coefficient $\left(\frac{K_{T+10}}{K_T}\right)$ is small being of the order of 1·15 − 1·20.

TABLE XXI.

Effect of varying the intensity of radiation.

Region = 366 $\mu\mu$. Temp. = 30°.

	$I_{abs.}$	Glucose.	H_2O_2.	HCl.	Tungstate.	$K_{unimol} \times 10^5$.
I.	2030 ergs	0·025*M*	0·00927*M*	0·0390 *N*	0·00820*M*	5·01
	505	,,	,,	,,	,,	2·53
II.	2030	,,	0·0121	,,	,,	5·01
	505	,,	,,	,,	,,	2·48

It will be seen from the above table that the velocity constants vary as the square root of the intensity of absorbed radiation in the ultraviolet.

Quantum Efficiency of the Process.—The quantum efficiency of the photo-oxidation was similarly calculated as in Section *A*. They are given in Tables XVII and XVIII. The quantum efficiency of the photo-oxidation at 366$\mu\mu$ is always greater than that at 750$\mu\mu$ – 600$\mu\mu$, as is to be expected. The reaction has the following characteristics :

(1) At 366$\mu\mu$, for relatively high concentration of H_2O_2, the reaction is zeromolecular with respect to H_2O_2 but for lower concentrations of H_2O_2 it is unimolecular, while at 600$\mu\mu$—750$\mu\mu$ where the absorption is due to chromium atom of the complex, the reaction always obeys the zeromolecular law.

(2) At 366$\mu\mu$, the velocity of reaction is proportional to the square root of the intensity of absorbed radiation, while at 600—750$\mu\mu$ (red region) it is directly proportional to the intensity of absorbed radiation.

(3) At 366$\mu\mu$, quantum efficiency is sometimes greater than unity but at 600$\mu\mu$—700$\mu\mu$ it is always much less than unity, it being much smaller than that at 366$\mu\mu$.

(4) That inverse of the velocity constant plotted against the inverse of the concentration of the reductant is always a straight line.

It is clear from the above that the chromium pertungstate is simply activated by red light, whereas it is decomposed by a quantum of ultraviolet light.

The reaction mechanism in red light is given thus :—

The whole of the absorbed radiation is available for the activation of chromic pertungstate.

$$\text{Chromic pertungstate (activated)} + \text{glucose} \longrightarrow \text{chromic tungstate} + \text{oxidation product} \quad \ldots \quad (i)$$

$$\text{Chromic pertungstate (activated)} \longrightarrow \text{chromic pertungstate (normal)} \quad \ldots \quad (ii)$$

$$\frac{dx}{dt} = K_t \frac{I}{h\nu} \cdot \frac{C_{s(G)}}{K_2 + K_1 C_{s(G)}}$$

where $C_{s(G)}$ is the surface concentration of glucose.

The quantum efficiency must here necessarily be less than unity.

A quantum of ultraviolet radiation, since it is able to start a chain reaction, may give a quantum yield higher than unity as has been actually observed.

$C_{s(G)}$ is again given by $\dfrac{K' C^{G}_{\text{Bulk}}}{K'' + K' C^{G}_{\text{Bulk}}}$ (Langmuir)

which shows that $1/c$ plotted against $1/K$ should be a straight line, as has been experimentally realised.

F. Vanadic Acid Sol as Photosensitiser.

The vanadic acid sol was prepared by the action of acetic acid on sodium vanadate. The p_H value of the sol was determined electrometrically using quinhydrone electrode.

Table XXII shows that a definite quantity of vanadic acid sol liberates the same amount of iodine from KI.

TABLE XXII.

$NaVO_3 = 0{\cdot}033M$. Acetic acid $= 0{\cdot}018M$. $p_H = 6{\cdot}0$.

Time in min.	C. c. thiosulphate (0·0093N) = iodine liberated by 0·3 c. c. of the sol solution.
0	2·24
60	2·24
180	2·25
480	2·26

In a mixture of vanadic acid sol and hydrogen peroxide, the total amount of iodine liberated from KI is equivalent to the sum of vanadic acid and hydrogen peroxide.

TABLE XXIII.

H_2O_2.	$NaVO_3$.	p_H of the solution (regulated by acetic acid).	C. c. thiosulphate ≡ iodine liberated by 0·4 c. c. of the mixture.
0·01*M*	0	5·0	0·85
0	0·033*M*	5·0	2·72
0·01	0·033	5·9	3·56

There was no dark reaction when hydrogen peroxide, glucose and vanadic acid sol in acid medium containing acetic acid were kept in the dark for 12 hours.

TABLE XXIV.

Effect of varying the concentration of hydrogen peroxide.

$I_{abs.}$ = 1256 ergs. Region = 366$\mu\mu$. Temp. = 27°. d = 1 cm.

Vanadate.	Acetic acid.	Glucose.	p_H.	H_2O_2	K_0 (g. mols transformed in unit time in a unit cell)	Quantum efficiency.
0·033*M*	0·018*M*	0·05*M*	5·0	0·012*M*	$5·17 \times 10^{-10}$	1·35
,,	,,	,,	,,	0·0156	$5·40 \times 10^{-10}$	1·41
,,	,,	,,	,,	0·023	$5·40 \times 10^{-10}$	1·41

It will be seen from Table XXIV, that the reaction follows the zero-molecular law with respect to H_2O_2. The reaction is attended with a large period of induction.

TABLE XXV.

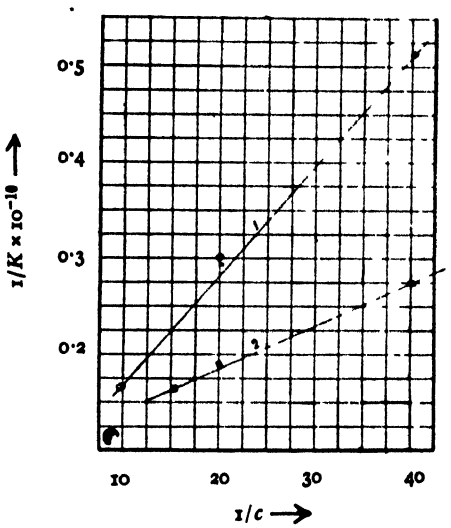
Effect of varying the concentration of glucose.

Temp. = 27°. $I_{abs.}$ = 1256 ergs.

Vanadate.	Acetic acid.	Glucose.	p_H.	H_2O_2.	$K_0 \times 10^{10}$.
0·033 *M*	0·018 *N*	0·065*M*	5·0	0·0125*M*	5·89
,,	,,	0·05	,,	,,	5·17
,,	,,	0·025	,,	,,	3·62

$1/K$ when plotted against $1/c_{glucose}$ gives a straight line (Fig. 3).

FIG. 3.



Curves 1 and 2 refer respectively to activated and nonactivated sol.

TABLE XXVI.

Effect of varying the concentration of sodium vanadate.

Temp. = 27°. I_{abs} = 1256 ergs per cm². per sec.

Vanadate.	p_H.	Glucose.	H_2O_2.	$K_0 \times 10^{10}$.
(*a*) 0·05*M*	5·0	0·05 *M*	0·012 *M*	5·69
(*b*) 0·033	5·0	0·05	,,	5·17

Under otherwise identical conditions, the velocity constant diminishes very slightly as the concentration of sodium vanadate diminishes.

TABLE XXVII.

Effect of varying the concentration of acetic acid.

Temp. = 28°. I_{abs} =4280 ergs per sq. cm. per sec.

Vanadate.	Acetic acid.	p_H.	Glucose.	H_2O_2	$K_0 \times 10^{10}$.
0·033 *M*	0·036*M*	4·5	0·025*M*	0·012*M*	5·17
,,	0·018	5·0	,,	,,	6·20

The velocity constant diminishes as the p_H of the reacting system diminishes.

Temperature Coefficient.—The temperature coefficient is small being of the order of 1·2 – 1·3.

TABLE XXVIII.

Effect of varying the intensity of absorbed radiation.

Temp. = 28°. $\lambda = 366\ \mu\mu$.

$I_{abs.}$	Vanadate.	Acetic acid.	p_H.	Glucose.	H_2O_2.	$K_0 \times 10^{10}$.
4280	0·033*M*	0·018*M*	5·0	0·025*M*	0·012*M*	6·20
1256	"	"	"	"	"	3·62

Table XXVIII shows that the velocity constant is proportional to the square root of absorbed intensity.

Quantum Efficiency of the Process.—Quantum efficiency of the process was calculated as in Section A. γ (Quantum efficiency) is generally greater than unity varying from 1 to 2.

Any mechanism of reaction that may be proposed for this photochemical oxidation should be in a position to explain the following facts:—

(1) The velocity of reaction is zeromolecular with respect to H_2O_2.

(2) The velocity of reaction is proportional to the square root of the intensity of absorbed radiation.

(3) The quantum efficiency is generally greater than unity, calculated on the assumption that the whole of the absorbed radiation is available for photo-activation.

(4) That the inverse of velocity constant plotted against the inverse of the concentration of the reductant is a straight line.

(5) Temperature coefficient is small but of the order of 1·2 – 1·3.

Assuming that the photochemical reaction takes place only between the molecules of glucose and pervanadate adsorbed on the surface of micelles of vanadic acid, and that the mechanism is the same as in the corresponding oxidations by H_2O_2 with tungstic acid as photosensitiser at 366$\mu\mu$ (Section A) we arrive at the equation of the velocity of reaction = dx/dt

$$= \sqrt{\frac{\bar{I}}{K_5\, h\nu}} \cdot K_2 C_{S\,[PV]} \quad \frac{K_4\, C_G^S}{K_3 + K_4\, C_G^S}$$

where $C_{S\,[PV]}$, C^{S}_{G} are the surface concentrations of pervanadate and glucose respectively.

It appears that the absorption capacity of vanadic acid micelle for pervanadic acid molecules will always be very large, so that the latter molecules always saturate the surface layer, and we get a zeromolecular velocity constant.

$$\text{Again} \qquad C^{S}_{G} = \frac{K_6\, C^{R}_{\text{Bulk}}}{K_7 + K_6\, C^{R}_{\text{Bulk}}}$$

so that by plotting $1/K$ against $1/c_{\text{bulk}}$ we should get a straight line as has been experimentally realised.

Induction Period.—Vanadic acid sol, prepared by the action of acetic acid on sodium vanadate was first exposed to ordinary ultraviolet rays (366 $\mu\mu$) for 4 hours, then immediately mixed with other components of the reacting system and exposed.

TABLE XXIX.

Effect of changing the concentration of H_2O_2.

Region = 366$\mu\mu$. Temp. = 26°.

$I_{\text{abs.}}$ = 1027 ergs. per cm.^{2}/sec. = $3{\cdot}1 \times 10^{-10}$ Einstein.

Na-vanadate.	Acid.	p_H.	Glucose.	H_2O_2.	$K_0 \times 10^{10}$	γ.
0·033M	0·018M	5·0	0·025M	0·03M	4·96	1·60
,,	,,	,,	,,	0·0155	4·60	1·48
,,	,,	,,	,,	0·0123	4·67	1·50
,,	,,	,,	,,	0·0009	5·06	1·63

In this reaction with pre-activated sol, induction period which was not prominent before completely disappeared. The velocity of reaction is here again zeromolecular with respect to H_2O_2 and under similar conditions of experiments the velocities observed are nearly the same as observed with sol not pre-activated.

G. *Chromic Hydroxide Sol as Photosensitiser.*

Preparation of Chromic Hydroxide Sol.—To the boiling chromic chloride solution, powdered ammonium carbonate was added to neutralise the free hydrochloric acid. The addition of ammonium carbonate to the boiling chromic chloride solution was stopped when a small quantity of chromic hydroxide was precipitated. Chromic chloride was then added drop by drop so as to peptise the precipitated chromic hydroxide. During the addition of chromic chloride solution, the liquid was boiled and shaken vigorously. The whole liquid was then dialysed at a temperature of 70°-80°, for 24 hours whereby greenish chromic hydroxide sol was obtained. The p_H of the sol was found to be 5·2 with quinhydrone electrode. The reaction does not take place at a much lower value of p_H .

No decomposition of hydrogen peroxide was observed in presence of chromic hydroxide sol at 579$\mu\mu$ when the concentration of hydrogen peroxide was smaller than that of chromic hydroxide. Chromic hydroxide reacts with hydrogen peroxide to form per-compounds. These additive compounds with hydrogen peroxide can not be removed as such by a process of dialysis. Hence it is surmised that the hydrogen peroxide complex remained adsorbed on the micelles of the chromic hydroxide. The dark reaction was found to be negligible.

TABLE XXX.

Region = 579$\mu\mu$. Temp. = 26°. $I_{abs.}$ = 800 ergs.

Glucose	H_2O_2.	Chromic hydroxide.	K (unimolecular with respect to H_2O_2).
0·025*M*	0·015*M*	0·0211*M*	$12{\cdot}5 \times 10^{-5}$
,,	0·0113	,,	$11{\cdot}32 \times 10^{-5}$

The above table shows that the reaction is unimolecular with respect to hydrogen peroxide.

H. *Molybdic Acid Sol as Photosensitiser and Ethyl Alcohol as Reductant.*

Reaction with Non-activated Sol.—A mixture of alcohol, hydrogen peroxide, hydrochloric acid and ammonium molybdate does not react when kept in the dark for 10 hours.

TABLE XXXI.

Region $= 366\mu\mu$.

$I_{abs.} = 1317$ ergs. Ammonium molybdate $= 0{\cdot}05M$. $HCl = 0{\cdot}0746N$. $EtOH = 4{\cdot}346M$. $H_2O_2 = 0{\cdot}025M$. Thiosulphate $= 0{\cdot}01N$.

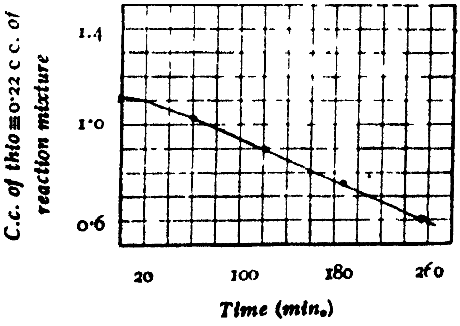
Time in min.	Time interval.	C.c of thio ≡ 0·22 c c. of reaction mixture.	Titre differ.	$K_0 \times 10^{10}$.
0		1·1		
		7·02 (Induction period)		
60	60			
120	60	0·9	0·12	7·58 (from 2 & 3)
186	66	0·76	0·14	7·80 (from 2 & 4)
251	65	0·61	0·15	8·11 (from 2 & 5)

From the above table it is clear that there is an induction period at the beginning and it is only after the lapse of this period that the reaction is zeromolecular.

$$\frac{dx}{dt} = K_0 \text{ (expressed in g. mols. transformed per sec. in a unit cell).}$$

This is more clearly brought out by plotting dx/dt against time (Fig 4) The straight portion of the graph after the induction period indicates a constant value of dx/dt.

FIG. 4.



Reaction with Pre-activated Sol.—Here the molybdic acid sol was first exposed to ultraviolet light for a sufficiently long time (about 3 hours) and then mixed immediately with other components of the reacting system. The induction period disappeared in this case.

TABLE XXXII.

All the factors same as in Table XXXI.

	Time in min.	Time interval.	C.c. of thio ≡ 22 c.c. of reaction mixture.	Titre difference.	$K_\theta \times 10^{-10}$.
1	0		1·24		
2.	68	68	1·09	0·15	8·35 (from 1 & 2)
3.	109	41	0·99	0·10	8·69 (from 1 & 3)
4.	203	94	0·78	0·21	8·58 (from 1 & 4)
5.	242	39	0·70	0·08	8·46 (from 1 & 5)

Reactions with pre-activated sol retained the same order (zeromolecular) as in the case of non-activated sol.

TABLE XXXIII.

Effect of varying the concentration of hydrogen peroxide.

$I_{abs.}$ at 366$\mu\mu$ = 1317 ergs = $4{\cdot}023 \times 10^{-10}$ Einstein. γ = Quantum efficiency. $d = 0{\cdot}5$ cm. EtOH = 4·346*M*. Molybdate = 0·05*M*.

H_2O_2.	HCl.	$K_\theta \times 10^{10}$ (non-activated).	γ (non-activated).	$K_\theta \times 10^{10}$ (activated).	γ (activated).
0·013*M*	0·0746*N*	7·61	0·95	7·95	0·99
0·0157	"	7·35	0·92	7·95	0·99
0·021	"	7·58	0·94	8·03	1·00
0·025	"	7·80	0·97	8·52	1·06

The above table shows that the reaction is zeromolecular with respect to hydrogen peroxide.

TABLE XXXIV.

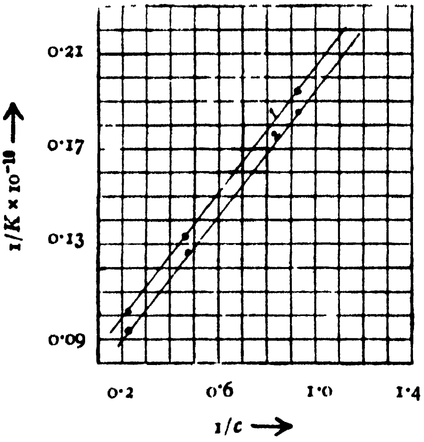
Effect of varying the concentration of alcohol.

$I_{abs.}$ = 1636·0 ergs.

Alcohol.	HCl.	Molybdate.	H_2O_2.	$K_0 \times 10^{10}$ (non-activated).	$K_0 \times 10^{10}$ (activated).
4·346*M*	0·0746*N*	0·05*M*	0·022*M*	9·8	10·6
2·173	,,	,,	,,	7·52	7·94
1·087	,,	,,	,,	5·19	5·43

$1/K$ graphically plotted against $1/c$ (alcohol) gives a straight line (Fig. 5).

FIG. 5.



Curves 1 and 2 refer respectively to non-activated and activated sol.

TABLE XXXV.

Effect of varying the concentration of hydrochloric acid.

HCl.	Molybdate.	H_2O_2.	Alcohol.	$I_{abs.}$	$K_0 \times 10^{10}$.
0·297*N*	0·05*M*	0·021*M*	4·346*M*	1317 ergs	4·96
0·148	,,	,,	,,	,,	5·07
0·0746	,,	,,	,,	,,	7·58
0·05	,,	,,	,,	,,	8·48

TABLE XXXVI.

Effect of varying the concentration of molybdate.

Molybdate.	H_2O_2	Alcohol.	p_H.	$I_{abs.}$ (Q)	$K_0 \times 10^{10}$.	$K/Q \times 10^{13}$.
0·05*M*	·027*M*	4·346	2·7	1636 ergs	10·10	6·18
0·025	,,	,,	,,	1365	8·35	6·12

The velocity of reaction is practically independent of the molybdic acid sol.

TABLE XXXVII.

Effect of varying the intensity of radiation.

$I_{abs.}$	Alcohol.	HCl.	Molybdate.	H_2O_2.	$K_0 \times 10^{20}$.
1404·8	4·326*M*	0·0746*N*	0·05*M*	0·025*M*	8·45
724·3	,,	,,	,,	,,	4·66
1404·8	,,	,,	,,	0·022	8·07
724·3	,,	,,	,,	,,	4·39

The zeromolecular velocity constant is directly proportional to the intensity of absorbed radiation.

Quantum Efficiency of the Process.—The quantum efficiency of the reaction is of the order of unity.

Temperature Coefficient.—The temperature coefficient $\left(\frac{K_{T+10}}{K_T}\right)$ is of the order of unity.

The photochemical reactions described in this section have the following characteristic features :—

(1) The reaction is zeromolecular with respect to H_2O_2.

(2) The reaction is independent of the concentration of molybdic acid sol.

(3) With the increase in the concentration of the reductant, the velocity constant increases, $1/K$ plotted against $1/c$ gives a straight line.

(4) The temperature coefficient of the reaction is unity.

(5) The quantum efficiency is approximately unity.

The whole of the absorbed radiation is available for the activation of molecules of permolybdate absorbed on the surface of micelles of molybdic acid.

The rate of reaction between the activated permolybdate molecules and the alcohol molecules is given by

Permolybdic acid + $h\nu \longrightarrow$ permolybdic acid (active) ... ... (*i*)

Permolybdic acid (active) $\longrightarrow$ permolybdic acid (normal) ... ... (*ii*)

Permolybdic acid (active) + alcohol $\longrightarrow$ oxidised product ... ... (*iii*)

$$I/h\nu = K_2[\mathrm{PM}]_{\mathrm{active}} + K_3[\mathrm{PM}]_{\mathrm{active}}\, C^{s}_{R}$$

where C^{s}_{R} is the surface concentration of reductant (alcohol).

Hence
$$[\mathrm{PM}]_{\mathrm{active}} = \frac{\frac{I}{h\nu}}{K_2 + K_3 \; C^{s}_{R}}$$

$$dx/dt = K \cdot \frac{I}{h\nu} \cdot \frac{C^{s}_{R}}{K_2 + K_3 \; C^{s}_{R}}$$

Now $C^{s}_{R} = \dfrac{K' \, C^{B}_{R}}{K'' + K' \; C^{B}_{R}}$ where C^{B}_{R} is the bulk concentration of the reductant.

For large values of C^{B}_{R}, C^{s}_{R} is large and in the limiting case the factor $\dfrac{K' \, C^{B}_{R}}{K'' + K' \; C^{B}_{R}}$ becomes unity. Then we have $\dfrac{dx}{dt} = \dfrac{I}{h\nu}$ and the quantum efficiency of the reaction is unity.

Again normally, $$dt/dx = \frac{h\nu}{I} \cdot \frac{K_2 + K_3 C_R^s}{K \cdot C_R^s}$$

$$= \frac{h\nu}{I} \cdot \frac{1}{C_R^s} + K_5$$

Under otherwise identical conditions, the inverse of velocity constant plotted against inverse of the concentration of reductant should give a straight line as has been experimentally observed.

In conclusion I would like to express my thanks to Prof. J. C. Ghosh for his kind interest in the work and to the Director of Public Instruction, Bengal for his kindly awarding me a Bengal Government Research Scholarship which enabled me to carry out this piece of investigation.

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Received July 27, 1936.

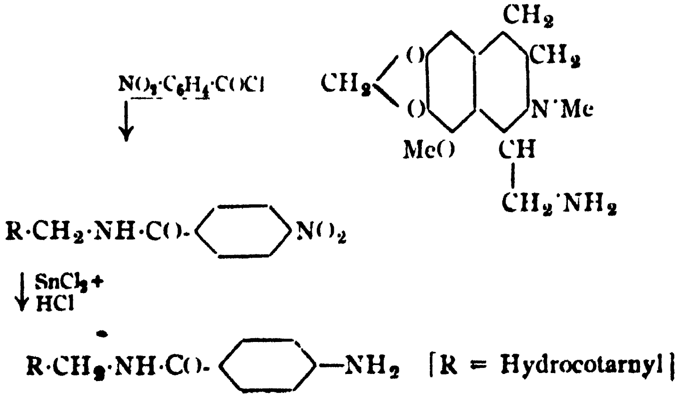
STUDIES IN THE COTARNINE SERIES. PART VIII. DERIVATIVES OF 1-AMINOMETHYLHYDROCOTARNINE.

By B. B. Dey and (Miss) P. Lakshmi Kantam.

The physiological action of some aminomethylhydrocotarnine derivatives has recently been studied by Magidson and Gorbowizki (*Ber.*, 1935, **68**, 656) who report that the compounds have strong mydriatic action. An investigation of the reaction between anhydrocotarninomethylamine and several nitro-aromatic acid chlorides, *e.g.*, *p*-nitrobenzoyl chloride and the reduction of the resulting compounds was undertaken in the hope that these products, on account of their analogy in structure to certain well known synthetic drugs like novocaine, etc., should develop important medicinal properties.

The observation of Magidson and his co-worker (*loc. cit.*) on the reduction of anhydrocotarninonitromethane by means of stannous chloride and hydrochloric acid to the methylamino compound as a pale yellow solid, m.p. 183°, could not be confirmed; the amine was always obtained as a yellow oil, an yield of 62% being realised by using zinc dust and alcoholic sodium hydroxide as a reducing agent (*cf.* Haworth and Perkin, *J. Chem. Soc.*, 1925, **127**, 1444).

The amine reacts at once with benzoyl chloride, *p*-nitrobenzoyl chloride, acetyl chloride, etc., in benzene solution, the hydrochloride separating out in quantitative yield. The free bases were prepared from the hydrochlorides by treating with strong ammonia for a long time. The reduction of the *p*-nitrobenzoylaminomethylhydrocotarnine into the amino compound was effected by shaking with stannous chloride and hydrochloric acid. The products which crystallised well from absolute alcohol were strong bases easily soluble in cold dilute acids to neutral solutions.


$NO_2 \cdot C_6H_4 \cdot COCl$
CH_2
O
O
CH_2
CH_2
N·Me
MeO
CH
$CH_2 \cdot NH_2$
$R \cdot CH_2 \cdot NH \cdot CO$
NO_2
$SnCl_2$ +
HCl
$R \cdot CH_2 \cdot NH \cdot CO$
$-NH_2$
[R = Hydrocotarnyl]

A detailed study of the pharmacological actions of these derivatives is being carried out in the Medical College, Madras.

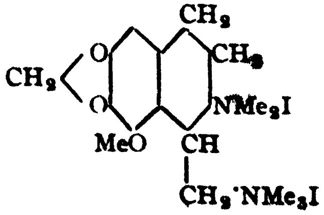
EXPERIMENTAL.

Anhydrocotarninonitromethane (Hope and Robinson, *J. Chem. Soc.*, 1911, **101**, 2114), crystallised from alcohol in colourless prisms melting at 129°. The yield is quantitative. It forms a sparingly soluble hydrochloride (m.p. 189°) with the colour changing to yellow at 150°, and a picrate (m.p. 136-37°).

Anhydrocotarninomethylamine (Haworth and Perkin, *loc. cit.*; Magidson and Gorbowizki, *loc. cit.*) was obtained by the reduction of anhydrocotarninonitromethane (5 g.) with zinc and sodium hydroxide in methyl alcoholic solution and working up in the usual way. It was obtained as a pale yellow oil (3·1 g.) which decomposed on distillation. The dihydrochloride was precipitated on saturating the ethereal solution of the base with dry hydrogen chloride. It is readily soluble in water and alcohol, m. p. 227°. It formed a *picrate* (m.p. 200°) and a sparingly soluble *sulphate* (m.p. 220°).

Benzoylaminomethylhydrocotarnine.— To the benzene solution of anhydrocotarninomethylamine, the required amount of benzoyl chloride was added with stirring. There was a vigorous reaction with evolution of heat and the hydrochloride of the benzoyl derivative quickly separated out. The solid was filtered after some time, washed well with dry benzene and the crude *hydrochloride* crystallised from hot water as colourless, hard, prismatic needles, m.p. 238-40°. The free base was liberated by keeping the hydrochloride in contact with strong ammonia. It crystallised from dilute alcohol in colourless thick rhombic plates, m.p. 125°. (Found: C, 67·3; H, 5·99; N, 7·99. $C_{20}H_{22}O_4N_2$ requires C, 67·79; H, 6·22; N, 7·91 per cent). The *picrate* crystallised from rectified spirit in short needles, m.p. 175-77°.

Action of Methyl Iodide on Anhydrocotarninomethylamine.



The amine was treated with excess of methyl iodide, when the reaction was instantaneous. The product was left overnight with some more of methyl iodide. The excess of methyl iodide was removed in vacuum and the solid was treated with cold water which dissolved most of it leaving a small amount of a thick oil. The clear yellow solution was evaporated in vacuum when the methiodide was obtained as a pale yellow crystalline hygroscopic solid, m.p. 135° (decomp.). (Found : I, 42·66. $C_{17}H_{28}O_3N_2I_2$, $2H_2O$ requires I, 42·45 per cent).

Acetylaminomethylhydrocotarnine.—The amine was treated with the required amount of acetyl chloride. The hydrochloride which separated in a crystalline state soon changed into an oily mass as it was very hygroscopic and absorbed moisture. It was dissolved in water and the yellow solution basified with caustic soda. The thick oil, which separated, solidified on washing with aqueous alcohol. It crystallised from 50% alcohol in colourless thin plates soluble in ether, m.p. 141°. (Found : N, 9·1. $C_{15}H_{20}O_4N_2$ requires N, 9·58 per cent).

p-*Nitrobenzoylaminomethylhydrocotarnine.* — *p*-Nitrobenzoyl chloride (2·6 g.), dissolved in benzene (10 c.c.), was slowly added to a solution of anhydrocotarninomethylamine (3·5 g.) in dry benzene (10 c.c.). The hydrochloride of the base separated almost immediately as yellow crystals. The crude hydrochloride, after washing with benzene and then with water and drying, weighed 4·5 g. The *hydrochloride* is practically insoluble in cold water but crystallises from boiling water in colourless prismatic needles, m.p. 234°. [Found : H_2O (at 110°/5mm.) 4·35. $C_{20}H_{21}O_6N_3$, HCl, H_2O requires H_2O, 3·97 per cent. Found : Cl (dried salt), 7·39. $C_{20}H_{21}O_6N_3$, HCl requires Cl, 8·14 per cent].

The free base was obtained from the powdered hydrochloride by keeping it in contact with strong ammonia for 24 hours. The solid changed at first into a sticky mass which slowly became granular. It was filtered, washed well with water and crystallised from hot rectified spirit as light yellow rhombic plates, m.p. 138°, yield 3·1 g. from 3·8 g. of the hydrochloride. (Found : N, 10·71. $C_{20}H_{21}O_6N_3$ requires N, 10·52 per cent). It formed a sparingly soluble *nitrate* (fern shaped crystals), m.p. 190°, and a *picrate*, m.p. 138°

p-*Aminobenzoylaminomethylhydrocotarnine.* — The foregoing nitro-compound (2·5 g.) was powdered and gradually added to a mixture of stannous chloride (9 g.), concentrated hydrochloric acid (25 c.c.) and a small piece of granulated tin and the whole shaken in a mechanical shaker for about 10 hours. Water (125 c.c.) was added, the clear liquid was basified with excess of 25% sodium hydroxide and the separated solid washed with water, dried on a porous plate and then in the desiccator and the dry solid extracted repeatedly either with warm benzene or absolute alcohol (60°). The amino-compound separated from the hot solvent in colourless, short prismatic rods, m.p. 185°. It dissolved in dilute hydrochloric acid to a clear solution and was reprecipitated unchanged on basification, yield 1·2 g. It formed a *picrate*, m.p. 167°, and a red dye when diazotised and coupled with β-naphthol. (Found : C, 64·89; H, 6·23; N, 11·09. $C_{20}H_{23}O_4N_3$ requires C, 65·04; H, 6·23; N, 11·39 per cent). The *acetyl* derivative separated from dilute alcohol in rectangular plates, m.p. 135°.

m - *Nitrobenzoylaminomethylhydrocotarnine* was prepared in the usual manner and crystallised from rectified spirit in light yellow rhombic plates, m.p. 95°. (Found : N, 10·56. $C_{20}H_{21}O_6N_3$ requires N, 10·52 per cent). The sparingly soluble *hydrochloride* crystallised from hot water containing a drop of hydrochloric acid in yellow, diamond-shaped plates, m.p, 185°. It formed a *picrate*, m.p. 196-98°.

m-*Aminobenzoylaminomethylhydrocotarnine*.—The reduction of the *m*-nitro-compound to the amino body was effected as in the other case with stannous chloride and hydrochloric acid. It crystallised from dilute alcohol in pale yellow thin plates, m.p. 80°. It dissolves readily in cold dilute acids and is recovered unchanged on basification. (Found : N, 11·81. $C_{20}H_{23}O_4N_3$ requires N, 11·38 per cent). On diazotising its solution in cold hydrochloric acid and coupling with β-naphthol, a deep red dyestuff was thrown down.

o - *Nitrobenzoylaminomethylhydrocotarnine* was prepared from anhydrocotarninomethylamine and *o*-nitrobenzoyl chloride. It crystallised from dilute alcohol in colourless prismatic needles, m.p. 143-45°. (Found : N, 10·88. $C_{20}H_{21}O_6N_3$ requires N, 10·52 per cent). The *hydrochloride* crystallised in short rectangular rods, m.p. 240° (decomp.). The *picrate* crystallised in prisms, m.p. 165°.

o-*Aminobenzoylaminomethylhydrocotarnine* was obtained as an oil by the reduction of the nitro-compound in the usual way. The *picrate* crystallised from methyl alcohol in rectangular plates, m.p. 175°. Diazotisation and coupling with β-naphthol gave a deep red dyestuff.

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THE ESTIMATION OF TOTAL VITAMIN C IN FOOD-STUFFS.

BY PRATUL NATH SEN-GUPTA AND B. C. GUHA.

Elsewhere (Guha and Pal, *Nature,* 1936, **137**, 946) we have given evidence to show that in many plant food-stuffs ascorbic acid is present partly in the combined state, from which the vitamin can be released readily by heating. It has been possible to extract this substance from several food-stuffs, which we have proposed to call " ascorbigen " for convenience. It has become clear from these results that the usual method of trichloroacetic acid extraction of food-stuffs, which has been almost universally used in the estimation of vitamin C by the Tillmans-Harris technique, would give low values for total ascorbic acid (combined and free) in many cases, where appreciable quantities of ascorbigen are present. From the nutritional standpoint it is necessary to know the amount of the total ascorbic acid, as we have previously observed (Guha and Pal, *loc. cit.*) that 0·2 % hydrochloric acid, which is normally present in gastric juice, is capable of splitting an aqueous extract of ascorbigen. It would appear, therefore, that many results so far recorded about the vitamin C content of food-stuffs, would in many instances give an erroneous idea about the total ascorbic acid available for nutritional purposes. Accordingly it was considered desirable to work out a method, by which the total ascorbic acid in food-stuffs might be estimated. The most reliable method must obviously be such as would split all the ascorbigen present and prevent the oxidation of ascorbic acid and thus give the highest value for ascorbic acid.

It should be stated that there is some controversy going on about the existence or otherwise of combined ascorbic acid in plant food materials (Mack, *Nature,* 1936, **138**, 505; Levy, *ibid.*, 1936, **138**, 933), but our evidence, which will be presented in greater detail later, shows almost conclusively that a reducing substance is released from cabbage by heat, which reduces the indophenol indicator like ascorbic acid. We are at present carrying out biological experiments to test whether this reducing substance is actually vitamin C. But so far as the object of the present paper is concerned, here it is intended to show merely that under certain conditions the value of ascorbic acid obtained is much higher than that obtained by the usual method. And if the titrimetric technique is considered to give the ascorbic acid value specifically, then the method elaborated in the present paper would appear to give the highest figure.

EXPERIMENTAL.

Determination of Total Ascorbic Acid without Reduction.

Five widely different varieties of food-stuffs were selected for study: *patol* (*Tricosanthes diocia*), cabbage, potato, guava and onion. 10 G. of each of the fresh food-stuffs were taken for each treatment, finely disintegrated in a mortar with washed sea-sand and mixed up with the appropriate extractant. The mixture was then centrifuged and the centrifugate diluted to 100 c.c. The titrations were carried out with the 2:6-dichlorophenol-indophenol indicator by the method described before (Ghosh and Guha, *J. Indian Chem. Soc.*, 1935, **12**, 30). Figures given in each table indicate the values obtained by the different treatments with the same sample of food-stuff. All experiments were carried out with three samples and in the tables all the three values are given. The experiments of each table are comparable among themselves as they were carried out under as identical conditions as possible.

(*a*) Table I gives the results obtained by treatment with trichloroacetic acid and hydrochloric acid of different concentrations for different periods. These indicate that treatment of 10 g. of food-stuff with 50 c.c. of 10% hydrochloric acid for 1 hour in CO_2 gives the highest figure for vitamin C, except in the case of the guava, which gives the best results with trichloroacetic acid.

(*b*) Table II gives the results obtained by treatment with 10% hydrochloric acid in CO_2 for different periods and also by treatment with 20% hydrochloric acid in CO_2. These figures show that the concentration of the acid remaining the same, the amount of ascorbic acid gradually diminishes with the increase of time; 20% acid apparently causes a loss except in the case of guava. Treatment with 10% hydrochloric acid for 1 hour in CO_2, therefore, seems to give the highest value in this group of experiments.

(*c*) 'In this set of experiments the effect of air, carbon dioxide and nitrogen on the value of ascorbic acid obtained in 10% hydrochloric acid solution was investigated. Nitrogen and CO_2 appear to be equally good, while there is a slight tendency to loss in air in one or two cases (Table III.)

(*d*) Finally, the results of treatment with 10% hydrochloric acid in CO_2 for 1 hour were compared with those obtained by heating the food-stuffs with water (50 c.c. per 10 g. of food-stuff) on a boiling water-bath for different periods in air, in CO_2, and in nitrogen and then extracting with trichloroacetic acid in the usual way (Table IV).

Figures are given in mg. of ascorbic acid per g. of food-stuff in all the tables. 10 G. of food-stuffs were taken in each case.

TABLE I.

Food-stuff.	Trichloro-acetic acid method.	50 C.c. of 10% tri-chloro-acetic acid.	50 C.c. of 1% HCl	50 C.c. of 5% HCl	50 C.c. of 10% HCl	50 C.c. of 1% HCl in CO_2 for 3 hrs.	50 C.c. of 5% HCl in CO_2 for 2 hrs.
			in CO_2 for 1 hour.				
Patol	0·138	0·155	0·109	0·147	0·156	0·136	0·145
	0·134	0·150	0·112	0·146	0·151	0·136	0.150
	0·138	0·150	0·112	0·147	0·155	0·138	0·149
Cabbage.	0·425	0·495	0·320	0·362	0·400	0·277	0·365
	0·300	0·272	0·239	0·352	0·452	0·274	0·380
	0·320	0·300	0·258	0·371	0·426	0·278	0·350
Potato	0·163	0·179	0·131	0·192	0·242	0·148	0·212
	0·153	0·173	0·130	0·180	0·226	0·138	0·204
	0·158	0·175	0·127	0·187	0·232	0·145	0·208
Guava	0·908	0·906	0·813	0·865	0·886	0·671	0·806
	0·900	0·905	0·788	0·885	0·852	0·668	0·803
	0·904	0·903	0·802	0·904	0·929	0·674	0·803
Onion	0·165	0·175	0·140	0·160	0·184	0·077	0·160
	0·165	0·171	0·142	0·161	0·186	0·068	0·153
	0·167	0·173	0·141	0·165	0·183	0·071	0.155

TABLE II.

Food-stuff.	Trichloroacetic acid method.	Treatment with 50 c.c. of 10% HCl in CO_2			50 C.c. of 20% HCl in CO_2 for 1 hr.
		for 1 hr.	for 2 hrs.	for 3 hrs.	
Patol	0·126	0·139	0·125	0·124	0·117
	0·128	0·147	0·129	0·127	0·122
	0·127	0·143	0·127	0·124	0·118
Cabbage	0·306	0·671	0·562	0·483	0·425
	0·315	0·600	0·520	0·416	0·350
	0·320	0·600	0·507	0·433	0·365
Potato	0·157	0·231	0·212	0·179	0·167
	0·160	0·226	0·206	0·176	0·170
	0·164	0·230	0·204	0·179	0·167
Guava	0·945	0·904	0·745	0·671	0·832
	1·040	0·945	1·040	0·800	1·040
	0·994	0·923	0·834	0·737	0·832
Onion	0·140	0·174	0·174	0·163	0·154
	0·152	0·179	0·166	0·159	0·151
	0·147	0·175	0·170	0·158	0·154

TABLE III.

Food-stuff.	Trichloroacetic acid method.	Treatment with 50 c.c. of 10% HCl in CO$_2$ for 1 hr.	N$_2$ for 1 hr.	air for 1 hr.
Patol	0·126	0·139	0·140	0·142
	0·128	0·147	0·145	0·146
	0·127	0·143	0·141	0·145
Cabbage	0·277	0·547	0·507	0·500
	0·292	0·600	0·547	0·533
	0·320	0·600	0·520	0·483
Potato	0·157	0·231	0·226	0·226
	0·160	0·226	0·221	0·231
	0·164	0·230	0·222	0·227
Guava	0·945	0·904	0·945	0·866
	1·040	0·945	0·951	0·863
	0·994	0·923	0·945	0·868
Onion	0·140	0·174	0·173	0·176
	0·152	0·179	0·175	0·168
	0·147	0·175	0·177	0·165

TABLE IV.

	Trichloroacetic acid method.	Treatment with 50 c.c. of water on boiling water-bath in N$_2$ for 10 mins.	air for 10 mins.	N$_2$ for 15 mins.	CO$_2$ for 15 mins.	N$_2$ for 20 mins.	50 C. c. of 10% HCl in CO$_2$ for 1 hr.
Patol	0.117	0·170	0·130	0·193	0·199	0·177	0·133
	0·128	0·181	0·128	0·201	0·201	0·184	0·138
	0·135	0·192	0·130	0·218	0·209	0·193	0·144
Cabbage	0·266	0·483	0·507	0·562	0·547	0·521	0·325
	0·281	0·547	0·408	0·671	0·630	0·407	0·341
	0·263	0·433	0·353	0.507	0·500	0·380	0·306
Potato	0·160	0·270	0·245	0·302	0·297	0·260	0·225
	0·150	0·272	0·247	0·304	0·295	0·267	0·225
	0·155	0·278	0·250	0·312	0·300	0·270	0·229
Guava	0·905	0·906	0·534	0·904	0·890	0·670	0·864
	0·904	0·903	0·531	0·901	0·887	0·675	0·868
	0·904	0·904	0·534	0·903	0·890	0·670	0·866
Onion	0·113	0·120	0·0710	0·120	0·119	0·117	0·115
	0·115	0·121	0·0714	0·121	0·119	0·119	0·117
	0.114	0·120	0·0713	0·125	0·122	0·119	0·117

Determination of Total Ascorbic Acid after Reduction

In the foregoing section the relative effects of different treatments on the ascorbic acid values of five different plant materials have been investigated, with reference to the question of estimation of the free ascorbic acid and of the ascorbic acid released from combination. It would seem, however, that the question of the naturally occurring dehydroascorbic acid should also be taken into consideration in order to get a true estimate of the total ascorbic acid from the nutritional standpoint, as dehydroascorbic acid does not reduce the dye but is known to be biologically potent. It is, therefore, necessary that the ascorbic acid values should be estimated after reduction of the reversively oxidised ascorbic acid by some suitable means. In order, therefore, to estimate the total ascorbic acid, comprising (1) the free ascorbic acid (2) the ascorbic acid released from combination by heat and (3) the ascorbic acid formed by the reduction of the dehydroascorbic acid, the five food materials were investigated after reduction with hydrogen sulphide on a boiling water-bath. Table V gives the relative values obtained (1) by the usual method of extraction with trichloroacetic acid (Ghosh and Guha, *loc. cit.*), (2) by heating the aqueous suspension on a water-bath in CO_2 for 15 minutes, (3) by passing H_2S into the aqueous suspension for 30 minutes, the suspension being heated in H_2S for 15 minutes out of this total period of 30 minutes, and (4) by passing H_2S into the aqueous suspension for 30 minutes at room temperature (25°). Hydrogen sulphide was, of course, completely removed by a current of CO_2 or N_2 before titration. It will be observed that, although in the previous section, heating in CO_2 gave the highest result, higher figures are obtained even by cold treatment with H_2S, which indicates the presence of reversively oxidised ascorbic acid in these materials. But still higher figures are obtained by treatment with H_2S in hot condition in the above five cases, except in guava. The difference between the values obtained by treatment with H_2S in the hot and cold conditions, incidentally, indicates the presence of ascorbigen especially in the cases of cabbage, *patol* and potato. However, considering all the different treatments, it is clear that the highest figures are obtained by treatment with H_2S in the hot condition. It should be mentioned that in these titrations, we have added 1 c.c. of *M*-formaldehyde (Mason, *J. Biol. Chem.*, 1930, **86**, 623) and 1 c.c. of glacial acetic acid to the dye before titration, in order to inhibit the effects of possible interfering substances.

In Table VI are given some figures obtained (1) by grinding the material under trichloroacetic acid, so as to inactivate the ascorbic acid oxidase as far as possible, (2) by heating the cut pieces in aqueous suspension in CO_2, (3) by treating the cut pieces in aqueous suspension with H_2S in the hot condition and (4) by first grinding up the cut pieces with sand and then heating in an atmosphere of H_2S as in experiment (3) In these experiments also the higher values were obtained by treating with H_2S in the hot condition and the fact that the values under (3) and (4) are identical show that it makes no difference whether the extraction is preceded by simple cutting up by scissors or by grinding with sand. It should be mentioned further that blank experiments with H_2S in the hot and cold conditions gave no values with the dye. The final method that we adopted is as follows:

The material (10 g.) was cut into small pieces, taken in a suspension of 50 c.c. of water and H_2S was passed into it. After 30-60 minutes, the suspension was heated under reflux on a boiling water-bath, while H_2S was being passed. Heating was continued for 15 minutes and then H_2S was removed completely (as tested by lead acetate paper) by a current of CO_2 or N_2. The suspension was then treated with 2·5 c.c. of 20% trichloroacetic acid, the mixture filtered or centrifuged and the filtrate made up to 100 c c. This solutiion was titrated against 0·5 c.c. of *M*/10-2:6-dichlorophenol-indophenol, to which 1 c.c. of *M*-formaldehyde and 1 c.c. of glacial acetic acid had been previously added. The titration should be finished within 1 minute.

TABLE V.

Food-stuffs.	Ascorbic acid by trichloro-acetic acid extraction.	Heated on a water-bath with 50 c.c. of water		Treated with 50 c.c. of cold water; H_2S passed for 30 mins. and H_2S removed by CO_2 or N_2.
		for 15 mins. in CO_2.	for 15 mins. in H_2S and H_2S removed by CO_2 or N_2.	
Cabbage	0·305	0·358	0·866	0·472
	0·208	0·260	0·743	0·371
	0·346	0·433	0·945	0·577
Patol	0·176	0.189	0·495	0·352
	0·186	0·212	0.547	0·384
	0·253	0·290	0·611	0·452
Potato	0·106	0·114	0·346	0·260
	0·110	0·125	0·400	0·358
	0·112	0·126	0·410	0·365
Guava	1·040	1·040	1·300	1·300
	1·600	1·500	1·890	1·890
	1·040	1·040	1·300	1·300
Onion	0·165	0·182	0·241	0·212
	0·155	0·176	0.241	0·208
	0.160	0·181	0·239	0·210

TABLE VI.

	(1)	(2)	(3)	(4)
Food-stuffs (10g.)	Treatment under trichloro acetic acid	The cut pieces heated with 50 c.c. of H_2O on a water-bath for 15 mins.		The cut pieces ground up with sand and then heated with water in presence of H_2S as in expt. 3.
		in CO_2.	in H_2S and H_2S removed by CO_2 or N_2.	
Cabbage	0·400	0·520	0·693	0·693
	0·650	0·750	0·866	0·866
Patol	0·433	0·495	0·611	0·611
	0·385	0·452	0·520	0·520
Potato	0·173	0·247	0·346	0·346
	0·176	0·267	0·358	0·358
Guava	1·500	1·500	1·890	1·890
	1·300	1·300	1·600	1·600
Onion	0·155	0·173	0·231	0·231
	0·165	0·182	0·247	0·247

DISCUSSION.

These results indicate that absolutely uniform results cannot be expected by the same treatment applied to widely different plant food-stuffs. Thus, while trichloroacetic acid treatment gives better results in the case of guava, hydrochloric acid gives higher values in other cases. Nor is there uniformity regarding the values obtained with different concentrations of hydrochloric acid. This does not seem surprising when it is considered that these food-stuffs contain perhaps many substances which might influence the behavior of vitamin C (free and combined) to various treatments and reagents. It should be mentioned that in cases where trichloroacetic acid and hydrochloric acid of different concentrations were used, blank experiments were carried out with the acids alone to see if they would decolourise the dye. It was found that if the titration was carried out within one minute under our conditions (Ghosh and Guha, *loc. cit.*) no material errors were introduced.

SUMMARY.

The general result of the investigation is that among the following methods (1) treatment with trichloroacetic acid, (2) allowing to stand with trichloroacetic and hydrochloric acids, (3) heating in CO_2 or N_2 for different periods, (4) treatment with H_2S in the cold and, (5) treatment with H_2S in the hot condition, the last method gave the highest value for ascorbic acid. This method would seem to give the total value of ascorbic acid comprising (*a*) the free vitamin, (*b*) the ascorbic acid which is released by heating, and (*c*) the reversively oxidised ascorbic acid.

A method has thus been elaborated which gives the highest ascorbic acid value and it would seem that many food-stuffs investigated before require re-investigation by the new technique for a more correct estimation of ascorbic acid. Although in some cases, as in guava, treatment with H_2S in the hot and cold conditions might give the same result, still it would seem desirable to carry out the treatment with H_2S in the hot condition as a routine procedure. There is the possibility that this treatment might itself release some non-specific reducing substance. This has been to some extent guarded against by adding formaldehyde to the dye. In this investigation it is, of course, assumed that the titrimetric technique carried out under precise conditions gives the correct value for ascorbic acid and we are at present planning biological experiments to test this point further.

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STUDIES IN THE COAGULATION OF COLLOIDS. PART XVI. FURTHER INVESTIGATION OF THE "ZONAL EFFECT" AND THE ANOMALOUS VARIATIONS OF THE VISCOSITY, TRANSPARENCY AND REFRACTIVITY DURING THE COAGULATIONS OF COLLOID ANTIMONY SULPHIDE BY AQUEOUS MERCURY CHLORIDE.

BY SHRIDHAR SARVOTTAM JOSHI AND T. MADHAVA MENON.

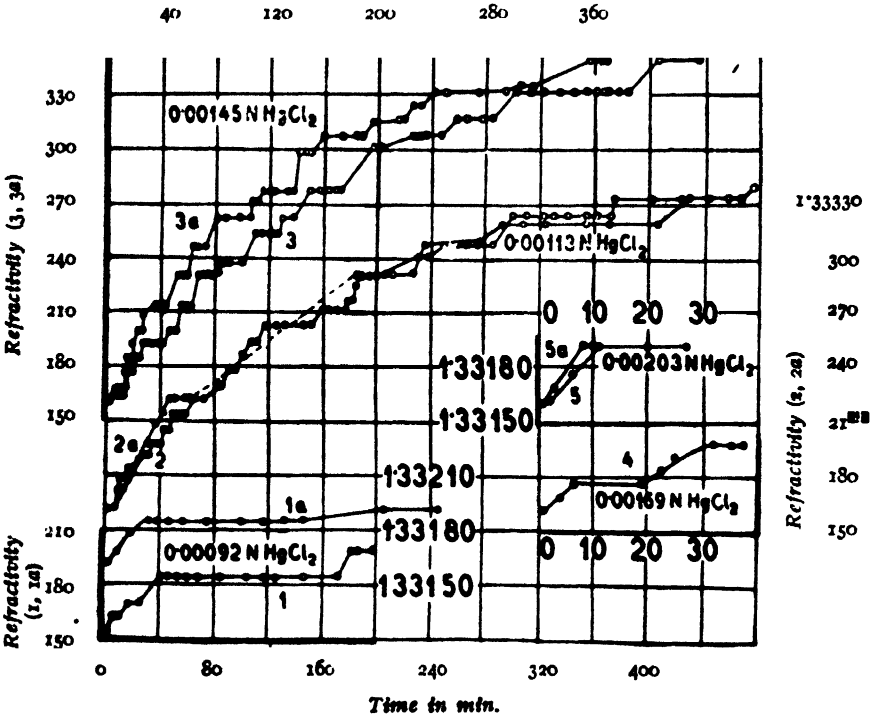
In Part XIV of this series (Joshi and Kulkarni, *J. Indian Chem. Soc.*, 1936, **13**, 439) it was reported that coagulations of colloid arsenious sulphide by aqueous *mercury chloride* showed a markedly unusual feature, *viz.*, that the viscosity, the transparency and opacity (measured independently from determinations of transparency) *remained almost constant during the coagulation time*. The familiar variations due to coagulation in these properties under the same conditions of experiment were observed when other electrolytes in appropriate amounts were used as coagulants, and also when but small amounts of any one of them were mixed with mercury chloride. In view of the definitely unusual character of these findings, it was considered desirable to examine this effect with a different system *viz.*, antimony sulphide sol. Furthermore, studies of the numerous coagulations of colloid manganese dioxide due both to electrolytes and oppositely charged sols (Joshi and Panikkar, *ibid.*, 1936, **13**, 309; Joshi and Jaya Rao, *ibid.*, 1936, **13**, 311; *Fettchem. Umsch.*, 1936, **43**, 36; *Kolloid Z.*, 1936, **76**, 145; *Current Science*, 1936, **4**, 481 ; Joshi and Purushottam, *ibid.*, 1936, **4**, 870) showed that the refractivity varied '*zonally*' in the *slow* region. This '*zonal effect*' was also observed in diverse coagulations of dilute oil suspensions by electrolytes (Joshi and Sarkar, *J. Bomb. Univ.*, 1935, **4**, 140) including mercury chloride, studied refractometrically. Experiments were also made, therefore, with colloid antimony sulphide employing the last named method of following a coagulation, as developed in these laboratories to investigate the generality of the '*zonal effect*' recorded, it would appear for the first time in the literature on coagulation kinetics, in Part XI of this series.

EXPERIMENTAL.

Colloid antimony sulphide was prepared as described earlier (Joshi and Prabhu, *J. Indian Chem. Soc.*, 1931, **8**, 11) and dialysed against repeated changes of distilled water till the dialysate was free from the acid. It was stocked in a carefully cleaned Jena bottle and its colloid content determined by Kessler's method (*Pogg. Ann.*, 1863, **118**, 17 ; *cf.* also Joshi and Prabhu, *loc. cit.*). Some of the typical results for the variation of n_D, the refractive index, due to different concentrations of the mercury chloride varied in the region 0·0009 to 0·002*N* during different coagulations, have been shown graphically in Fig. 1. It was found that under sensibly identical conditions of observation, the variation of n_D during a coagulation was not fully reproducible. Two of the results of such repeat experiments are

FIG. 1.

Variation of refractivity during coagulation.



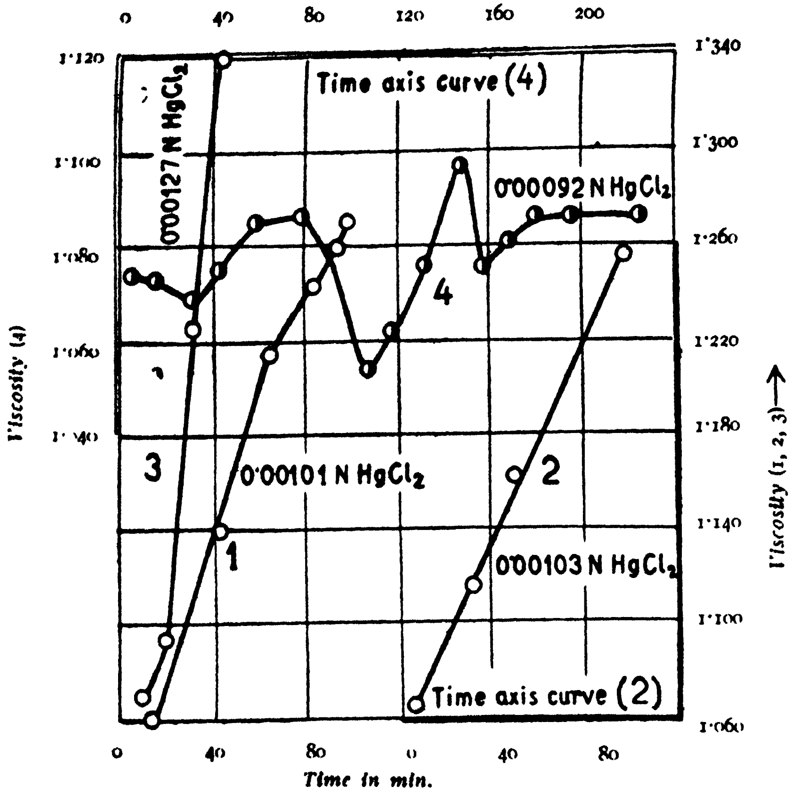
shown by curves 1, 1*a*, 2, 2*a*, 3, 3*a*, and 5, 5*a* in Fig. 1. In the coagulation corresponding to curve 2*a*, the observation of n_D was discontinued at the point (40, 160) and resumed at the point (160, 215). It will be seen, however, that the principal *zonal effect* in the time-variation of n_D during a given coagulation is sufficiently persistent and brought out by both series of the curves. The temperature of the coagulating system was maintained at 34±0·1°. The general procedure and precautions were the same as described previously (Joshi and Rao, *loc. cit.*). The variation of η, the viscosity of the same colloid in the presence of $HgCl_2$ was studied in the range 0·0009 to 0·0013*N* by Scarpa's method with modifications described previously (Joshi and Menon, *J. Indian Chem. Soc.*, 1933, **10**, 599). Only four typical curves for η-change are given in Fig. 2. Results for the change of intensity of light transmitted during the coagulation as recorded with a thermopile (*cf.* Joshi and Kulkarni, *loc. cit.*, also Joshi and Rao, *ibid.*, 1936, **13**, 311) are shown graphically in Fig. 3. In order to obtain confirmation of these results, transparency of the colloid was also measured by using a Duboscq colorimeter (*cf.* Joshi and Kulkarni, *loc. cit.*). The data are shown in Fig. 4. In order to prevent overlapping of the curves and especially to economise the figure space, different co-ordinate axes have been used for curves in a given series; their origin, position and the scale units have been indicated in the figure.

DISCUSSION.

The results for the variation of n_D, the refractivity during the coagulation of colloid antimony sulphide by mercury chloride as seen from curves in Fig. 1 are in complete agreement with earlier results mentioned in the introduction. Also, as found previously (Joshi and Rao, *Kolloid Z.*, *loc. cit.*; *J. Indian Chem. Soc.*, 1936, **13**, 311) on colloid manganese dioxide and dilute oil-suspensions (Joshi and Sarkar, *loc. cit.*) coagulated by different coagulants, comparison of curves 2, 2*a*, 3, 3*a* with 1, 1*a*, 4, 5 and 5*a* shows that *maximum zonal effect is observed only with moderate concentrations of the coagulant. For much larger and much smaller values of the last quantity, the net change in* n_D *as also the number of zones tends to diminish.* In this connection it is interesting to point out that in numerous measurements of different colloids, η, the viscosity, varied discontinuously or through a number of breaks in the *slow* region (Joshi and Viswanath, *J. Indian Chem. Soc.*, 1933, **10**, 329, ; Joshi and Menon, *loc. cit.*; Joshi and Nanjappa, *ibid*, 1934, **11**, 133 ; Joshi and Iyengar, *ibid.*, 1934, **11**, 555, 573 ; Joshi and Panikkar, *ibid.*, 1934, **11**, 797 ; *Proc. Acad. Sci. U. P.*, 1935, **5**, 41 ; *J. chim. phys.*, 1935, **32**, 455 ; Joshi and Sarkar, *loc. cit.*). The results now obtained confirm this. It is seen, for example, from Fig. 2 that while η rises pronouncedly in coagulations corresponding to curves 1, 2 and 3 in Fig. 2, the definite effect of any further diminishing the coagulant concentration is seen in the marked increase in the number of breaks or discontinuities as seen in curve 4, Fig. 2. The net increase in η due to coagulation is also much less in the latter than in *rapid* coagulations. It is seen therefore, that the influence of mercury chloride on n_D and η in the case of colloid antimony sulphide is analogous to that of other electrolytic coagulants in respect of the general finding in these laboratories, *viz.*, *the zonal character of a slow coagulation.* It must also be recorded at this stage that the previous result that mercuric chloride, whilst producing coagulation of colloid arsenious sulphide over the whole concentration range investigated definitely failed to produce a net rise of viscosity in by far the majority of cases studied (*cf.* Part XIV), does not find analogy with the colloid studied now.

FIG. 2.

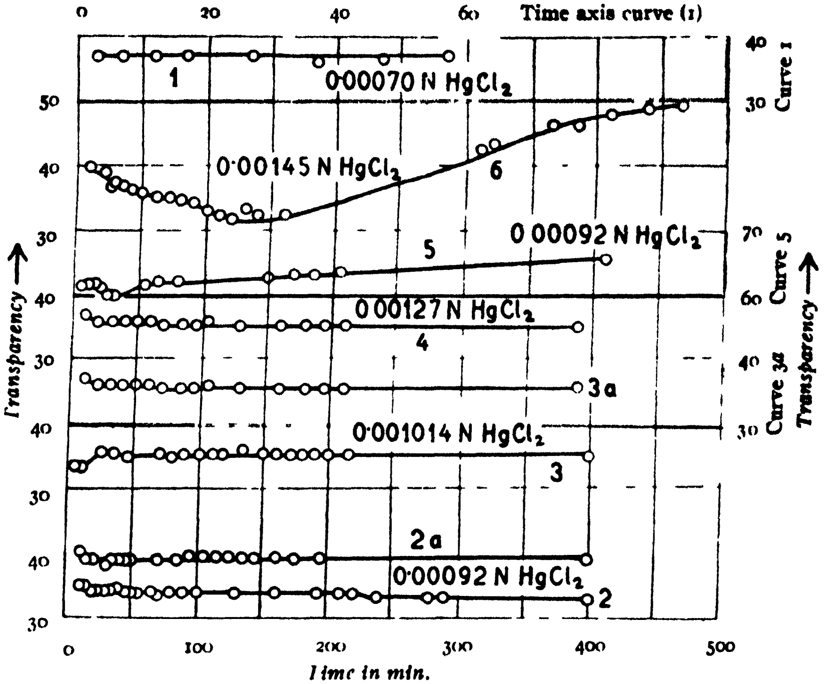
Variation of viscosity during coagulation.



A comparison of the curves in Figs. 3 and 4 for the variation of the transparency determined by thermopile and colorimeter respectively with ding curves for coagulations of colloid arsenious sulphide in the

FIG. 3.

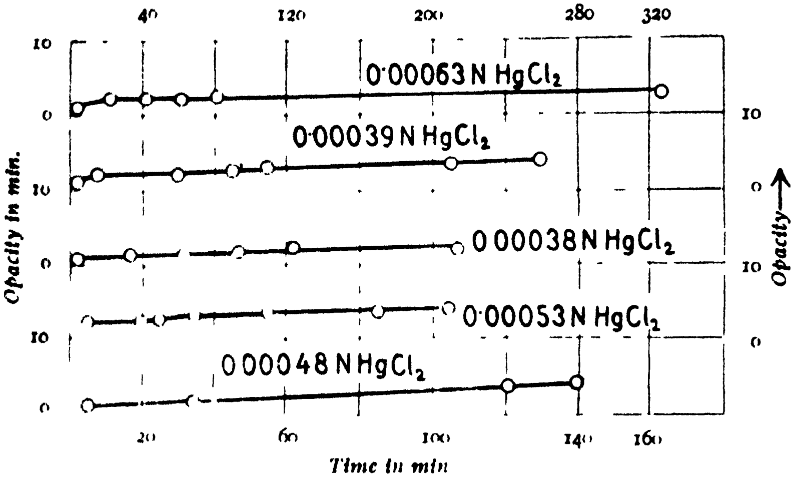
Variation of transparency during coagulation



presence of mercuric chloride reported earlier (Part XIV, *loc. cit.*), reveals that the above property varies in a way which depends upon the concentration of the coagulant. At low values of the last quantity, the transparency diminishes (Fig. 3) and the capacity increases (Fig. 4) during just the initial stage of coagulation ; they remain almost constant subsequently. During this time the process of coagulation had progressed producing perceptible flocculation, although the corresponding transparency and opacity (Figs. 3 and 4) had not changed in the familiar manner. The marked increase in transparency subsequent to its reaching a minimum in curve 6 in Fig. 3 corresponding to the maximum concentration of the coagulant employed was due to the settling of the coagulum produced by an appreciable flocculation during the latter stages. It is seen, therefore, that the anomalous behaviour of mercury chloride in failing to produce rise in opacity (and its reverse) in flocculations of colloid arsenious sulphide (*cf.* part XIV) is also observed in the case of the present sol as long as the concentration of the coagulant is low. This finding has a marked interest in relation to the occurrence of '*zones*' brought out especially by the refractivity measurements ; which suggest that *in the slow region* corresponding to the horizontal sections in the n_D -time curves (Fig. 1), *either* (*i*) the refractivity is invariant (or, at any rate has a markedly altered time-rate) despite the occurrence of coagulation, *or* (*ii*) that the coagulation comes to a standstill for a period, re-starts, to be followed by another phase of partial or almost complete inactivity and so on, periodically, till flocculation changes into the precipitation of the coagulum.

FIG. 4.

Variation of opacity during coagulation



SUMMARY.

1. The coagulation of colloid antimony sulphide has been followed in the *slow* region by observations of change of refractivity, viscosity, transparency and capacity in the presence of aqueous mercuric chloride. 2. Viscosity and *especially refractivity* changes show discontinuities or *zones of coagulation*, which become most conspicuous in the *medium slow region*. 3. Transparency (and the separately measured opacity) remains almost stationary except during initial stages, with small concentrations of the coagulant, which is partly similer to earlier results (Part XIV, in this series) on colloid arsenious sulphide with the same coagulant, when viscosity, transparency and opacity were found to be invariant over the whole range of the $HgCl_2$ concentrations examined.

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ON SYNTHETIC COUMARINS. PART I. COUMARINS DERIVED FROM RESACETOPHENONE.

By Radha Raman Agarwal and Sikhibhushan Dutt.

Pechmann's synthesis of coumarins (*Ber.*, 1883, **16**, 2119 *et seq*) from phenols and malic acid or acetoacetic ester is of a very general application and a large number of substituted coumarins have been synthesised using different phenols. Resorcinol under these conditions using malic acid gives 7-hydroxy-coumarin or umbelliferone, but coumarins derived from resacetophenone have not yet been prepared. Weiss and Woldich (*Monatsh.*, 1926, **47**, 427) however, condensed rasacetophenone with ethyl ethoxymethyleneacetoacetate in presence of sodium ethoxide and got a product which later on was found to be 7-hydroxy-3:6-diacetylcoumarin by Weiss and Merksammer (*Monatsh.*, 1928, **50**, 115).

In connection with the synthesis of cuscutalin, a coumarin derivative isolated from the stems of *Cuscuta reflexa*, Roxb. by the present authors (*J. Indian Chem. Soc.*, 1935, **12**, 384, 586) it was found necessary to prepare 6-acetyl-7-hydroxycoumarin. Recourse was taken to attempt nuclear acetylation through Friedel and Craft's reaction using coumarin or umbelliferone, but was not met with success. Hence snbstituted coumarins were prepared by the method of Pechmann (*loc. cit.*) starting with resacetophenone. Various condensing agents were employed but it was found that sulphuric acid or fused zinc chloride gives very poor yields, whereas sodium ethoxide was found to be the best for ethyl acetoacetate. In the case of snbstituted ethyl acetoacetates, if the reaction was done at low temperatures the yield obtained even with concentrated sulphuric acid was quite significant.

Clayton (*J. Chem. Soc.*, 1908, **93**, 2016) showed that the substituent group present in the nucleus of the phenol taking part in Pechmann's condensation greatly affects the reaction. He found that chlorophenol reacts with difficulty and gives a very poor yield, whearas a negative substituent like NO_2 or COOH totaly inhibits the condensation. Chakravarti and Ghosh (*J. Indian Chem. Soc.*, 1935, **12**, 622), however, proved that these generalisations of Clayton do not hold and they could smoothly condense chlororesorcinol or nitroresorcinol with alkyl-acetoacetic esters both in presence of sulphuric acid or phosphorus pentoxide. Clayton (*loc. cit.*) concluded that a negative substituent present in the neighbourhood of the hydroxyl of the phenol, not taking part in the condensation, has an inhibitive effect on the reaction. In resacetophenone the acetyl group is present in *ortho* position to the free hydroxyl group not taking part in the condensation and being sufficiently acidic does not make the phenol inert even if concentrated sulphuric acid is used as a condensing agent. But if this hydroxyl is surrounded by another hydroxyl group on the other side, as for example in gallacetophenone, condensation does not occur. These facts clearly show that the conclusions of Clayton are not of general application, for according to his views gallacetopenone should have condensed more easily than resacetophenone to form coumarins.

In the present paper resacetophenone has been condensed with malic acid, ethyl acetoacetate, ethyl methylacetoacetate, ethylethyl acetoacetate, ethyl *iso*propylacetoacetate and ethyl benzylacetoacetate. The acetyl derivative, oxime, semicarbazone and phenylhydrazone of 6-acetyl-7-hydroxy-4-methylcoumarin, derived from resacetophenone and ethyl acetoacetate, have also been prepared. The methyl group present in the acetyl radical of this coumarin being in the immediate neighbourhood of a carbonyl group is highly reactive and can condense with aromatic aldehydes by the method of Kostanecki and Tambor (*Ber.*, 1904, **37**, 773, 779) to form styryl ketones, analogous to chalkones derived from resacetophenone. Benzaldehyde has been condensed with 7-hydroxy-6-acetyl-4-methylcoumarin in this way to give 7-hydroxy-4-methylcoumarin-6-styrylketone and this interesting compound, which is much more coloured than the corresponding chalkones, gave all the reactions of chalkones. It is proposed to call this class of compounds coumaro-chalkones. Further work on these coumaro-chalkones is in progress and will be communicated shortly.

EXPERIMENTAL.

7-Hydroxy-6-acetylcoumarin.—Resacetophenone (1 g.), malic acid (0·85 g.) and concentrated sulphuric acid (4 g.) were warmed on an oil-bath till no effervescence took place. The mixture was left overnight and then poured over crushed ice. This was repeatedly extracted with chloroform and the chloroform extracts on concentration gave the coumarin as yellowish white amorphous mass. It was recrystallised from benzene and petroleum ether mixture as colourless flakes, m. p. 139°, yield 30%. (Found: C, 64·51; H, 4·20. $C_{11}H_8O_4$ requires C, 64·7; H 3·9 per cent).

7-Hydroxy-6-acetyl-4-methylcoumarin.—Resacetophenone (10 g.), ethyl acetoacetate (7·5 g.) and (3 g.) of sodium in 35 c.c. of absolute alcohol were refluxed over a water-bath for 4 hours, when the sodium salt of the coumarin began to separate gradually and the dark red colour of the reaction mixture faded to fluorescent pink. It was left overnight and then treated with distilled water, when a clear solution was obtained. On acidification a brown oil separated on the top, which was extracted with ether. The ethereal extracts were dehydrated and the solvent evaporated gradually when beautiful needles separated out, m.p. 140°. On recrystallisation from benzene buff coloured star-shaped needles were obtained, m.p. 147°, yield 90 %. It is soluble in ether, ethyl acetate, alcohol, pyridine and glacial acetic acid, less so in benzene and insoluble in petroleum ether. It gives a very light yellow colour with caustic alkalis and a purple violet colour with alcoholic ferric chloride (Found: C, 66·0; H, 4·91. $C_{12}H_{10}O_4$ requires C, 66·1; H, 4·6 per cent).

Resacetophenone (0·7 g.) ethyl acetoacetate (0·65 g.) and concentrated sulphuric acid (3 c.c.) were set aside overnight and worked up according to the method of Pechmann (*loc. cit*). The yield obtained was very poor but could be considerably improved if the reaction mixture was left in a frigidaire. Buff coloured needles from benzene, m. p. 146°, were obtained.

The Acetyl derivative.—The above coumarin (0·8g.), acetic anhydride (5 c.c.) and a few drops of pyridine were refluxed over a sand-bath and then decomposed with water. Colourless microcrystalline needles from alcohol were obtained, m.p. 120-21°. (Found: C, 64·05; H, 4·9. $C_{14}H_{12}O_5$ requires C, 64·6; H 4·6 per cent). Fused sodium acetate in place of pyridine led to uncrystallisable products.

The Oxime.—The coumarin (0·8 g.), dissolved in alcohol (25 c.c.), was heated with a solution of hydroxylamine hydrochloride (1 g.) in water (10 c.c.) and 0·6 g. of caustic potash in 5 c.c. of water over a water-bath for 3 hours. On distilling back the solvent and adding ice-cold water the oxime separated out as a white powder which on recrystallisation from ethyl alcohol gave white flakes, m.p. 205°. (Found: N, 6·5. $C_{12}H_{11}O_4N$ requires N, 6·0 per cent).

The Semicarbazone, prepared in the usual manner, crystallised from petroleum ether as shining colourless flakes, m.p. 183°. (Found: N, 15·88. $C_{13}H_{13}O_4N_3$ requires N, 15·3 per cent).

The Phenylhydrazone, prepared from phenylhydrazine and the coumarin in acetic acid, crystallised from acetic acid as pale yellow needles, m.p. 146-47°. (Found: N, 8·6. $C_{18}H_{16}O_3N_2$ requires N, 9·1 per cent).

7-Hydroxy-6-acetyl-3:4-dimethylcoumarin. — Resacetophenone (1 g.) ethyl methylacetoacetate (0·95 g.) and concentrated sulphuric acid (3 c.c.) were left overnight in a frigidaire at 5°. The mixture was then poured over crushed ice when an oil separated out which was taken up by ether. On removal of ether a brown crystalline mass was obtained which on recrystallisation from ethyl alcohol gave colourless silky needles, m.p. 168°, yield 50%. (Found: C, 66·75 ; H, 5·62. $C_{13}H_{12}O_4$ requires C, 67·2; H, 5·2 per cent).

7- *Hydroxy- 6-acetyl- 3 - ethyl- 4- methylcoumarin.* — Resacetophenone (1·5 g.), ethyl ethylacetoacetate (1·2 g.) and concentrated sulphuric acid (6 c.c.) were left in the frigidaire and treated as above. On recrystallisation from alcohol-ether mixture colourless slender shining needles were obtained, m.p. 122°, yield 40%. (Found: C, 68·0; H 5·5. $C_{14}H_{14}O_4$ requires C, 68·3; H 5·7 per cent).

*7-Hydroxy-6-acetyl-4-methyl-3-*iso*propylcoumarin.* — Resacetophenone (1·2 g), ethyl *iso*propylacetoacetate (1·2 g.) and concentrated sulphuric acid (5 c. c.) were treated as above. The chloroform extract gave a crystalline yellowish white stuff which on recrystallisation from ether gave clusters of soft colourless needles, m. p. 108° after previous softening at 100°, yield 20%. (Found : C, 68·75 ; H, 6·0. $C_{15}H_{15}O_4$ requires C, 69·2 ; H, 6·1 per cent).

7- *Hydroxy- 6- acetyl- 4- methyl- 3- benzylcoumarin.*— Resacetephenone (1 g.), ethyl benzylacetoacetate (1·2 g.) and concentrated sulphuric acid (4 c.c) were left overnight in the frigidaire. On pouring the mixture over crushed ice the coumarin separated out as a flocculent yellow precipitate. This was twice crystallised from ethyl alcohol when pale yellow plates, m. p. 170°, were obtained, yield 60%. (Found : C, 73·60 ; H, 5·52. $C_{19}H_{16}O_4$ requires C, 74·0 ; H, 5·2 per cent).

7-Hydroxy-4-methylcoumarin-6-styryl ketone or *7-Hydroxy-4-methylcoumaro-chalkone.*—7-Hydroxy-6-acetyl-4-methylcoumarin (1 g.) and benzaldehyde (0·5 g.) were mixed together in about 5 c. c. of alcohol, free from aldehyde, and treated with aqueous caustic potash (50%, 10 c. c.). The mixture was colourless at first and gradually became very intense yellow. It was left overnight in a warm place and then treated with cold dilute hydrochloric acid, when a yellow oil separated out which turned into flocculent mass on standing. This was then crystallised twice from 50% dilute acetic acid as bright yellow shining flakes, m.p. 141°, yield 75%. It gives a deep orange yellow colour with caustic alkalis, a delicate violet green colour with ferric chloride and the crystals are turned crimson and yield a yellow solution on adding concentrated sulphuric acid. (Found : C, 74·32 ; H, 4·8. $C_{19}H_{14}O_4$ requires C, 74·4 ; H, 4·6 per cent).

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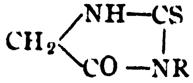
QUINOLINE DERIVATIVES. PART I.

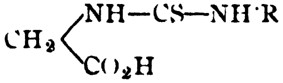
By Tejendra Nath Ghosh.

In a previous communication (Ghosh, *J. Indian Chem. Soc.*, 1934, **11**, 27) it has been shown that the thiohydantoin (I) condenses with *o*-nitrobenzaldehyde and the reduction of the resulting product yields a quinoline derivative.

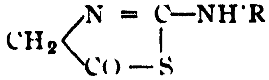


(I)

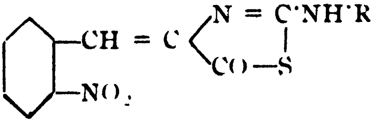
The thiohydantoin is readily hydrolysed by alkali to the corresponding thiocarbamidoacetic acid derivative (II). When treated with acetic anhydride, the compound (II) is readily converted into the thiazole derivative (III), which, because of the presence of a reactive methylene group, condenses with *o*-nitrobenzaldehyde to yield the compound (IV). The reduction of (IV) with zinc dust and acetic acid yields the quinoline derivative (V).



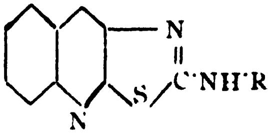
(II)



(III)



(IV)



(V)

Reference may be made to the pharmacological examination of thiazole derivatives (Suter and Johnson, *J. Amer Chem. Soc.*, 1930, **52**, 1585). 2-Thiocarbonyl-4-keto-5 : 5-diethyltetrahydrothiazole has been found to have a narcotic effect slightly greater than that of veronal but with a quicker recovery (Leonard, *Medd. K. Ventenskapsakad. Nobel-Inst.*, 1922, **4**, No. 14, 1-13). In view of the chemotherapeutical importance of thiazole derivatives and of the presence of thiazole ring in vitamin B_1 (Williams, *J. Amer. Chem. Soc.*, 1936, **58**, 1063 ; Williams and Cline, *ibid.*, 1936, 58, 1504), the present synthesis of thiazole-quinoline derivatives is of considerable interest. Compounds (III) and (V), (where R = phenetyl) have been synthesised. These compounds are expected to possess antipyretic and analgesic properties (*cf.* Suter and Johnson, *loc. cit.*).

EXPERIMENTAL.

p-*Tolylthiocarabamidoacetic Acid* (II, R=*p*-tolyl).—The compound (I, R=*p*-tolyl, 3·8 g.) was dissolved in alcohol (100 c. c.) containing 1·3 g. of caustic potash. The rose-coloured clear solution was heated under reflux for about 1 hour and evaporated to dryness. The solid obtained was the potassium salt of *p*-tolylthiocarbamidoacetic acid. The *free acid* was obtained as a colourless precipitate when a cold aqueous solution of the potassium salt was acidified with dilute hydrochloric acid. It crystallised from hot water in colourless rectangular plates, m. p. 147-148° (decomp.), yield 3 g. (Found : N, 12·35. $C_{10}H_{12}O_2N_2S$ requires N, 12·50 per cent). It is soluble in sodium bicarbonate solution.

2-*Keto*-5-*p*-*tolylaminodihydro*-1 :4-*thiazole* (III, R=*p*-tolyl).—An acetic anhydride solution of the above compound (II, *p*-tolyl) was heated under reflux for about 1 hour and cooled, when a crystalline precipitate came out, which further crystallised from alcohol in brownish plates, m. p. 157-58°, yield almost quantitative. (Found : N, 13·27. $C_{10}H_{10}ON_2S$ requires N, 13·59 per cent). It is not desulphurised by yellow oxide of mercury, indicating that the sulphur atom is cyclic. It is insoluble in cold alkali but on long standing goes into solution and the alkaline solution, on acidification, yields the original acid (II, R=*p*-tolyl).

2-*Keto*-3-o-*nitrobenzal*-5-p-*tolylaminodihydro*-1 : 4-*thiazole* (IV, R=*p*-tolyl).—An acetic anhydride solution of the compound (III, R=*p*-tolyl, 6·2 g.) and *o*-nitrobenzaldehyde (4·5 g.) was heated under reflux for about 2 hours. The clear solution, on cooling, deposited a crystalline mass which further crystallised from glacial acetic acid in yellowish needles, m. p. 200-201°, yield 7 g. (Found . N, 12·18. $C_{17}H_{13}O_3N_3S$ requires N, 12·39 per cent).

Reduction of the above Compound (IV, R=*p*-tolyl) : *Formation of* 5-p-*Tolylaminothiazole*-2 : 3 (2′ : 3′)-*quinoline* (V, R=p-*tolyl*).—A solution of the above compound (IV, R=*p*-tolyl, 6 g.) in acetic acid (100 c. c.) was boiled with zinc dust until it became colourless ; it was then filtered and diluted with much water. The solid, thus obtained, was filtered, extracted with hot alcohol, washed with dilute hydrochloric acid and water and was finally crystallised from alcohol in colourless plates m. p. 191-92°, yield 0·5 g. (Found : N, 14·22. $C_{17}H_{13}N_3S$ requires N, 14·43 per cent). It is soluble in strong acids but insoluble in alkali.

The same compound (m. p. 191-192°) is obtained, if the reduction is carried out with granulated tin and hydrochloric acid.

p-*Phenetylthiocarbamidoacetic Acid* (II, R = *p*-phenetyl).—A dilute alcoholic solution of glycine (2·3 g.) and *p*-phenetyl*iso*thiocyanate (5·4 g.) was heated under reflux for about an hour and then evaporated almost to dryness. The solid was then treated with cold dilute alkali ; the rose coloured alkaline solution, on acidification with hydrochloric acid, gave a precipitate which crystallised from alcohol in colourless rectangular plates, m. p. 134-35° (decomp.), yield 4·5 g. (Found : N, 10·85. $C_{11}H_{14}O_3N_2S$ requires N, 11·02 per cent). It is readily soluble in aqueous sodium bicarbonate solution.

2-Keto-5-p-*phenetylaminodihydro-1:4-thiazole* (III, R = *p*-phenetyl).—The method of preparation was the same as in the case of the previous compound (III, R = *p*-tolyl). The compound crystallised from glacial acetic acid in brownish rectangular plates, m. p. 193-94°. (Found : N, 11·61. $C_{11}H_{12}O_2N_2S$ requires N, 11·86 per cent). It is insoluble in alkali and is not desulphurised by yellow oxide of mercury.

*2-Keto-3-*o*-nitrobenzal-5*-p-*phenetylaminodihydro-1:4-thiazole* (IV, R = *p*-pheuetyl).—The method of preparation was the same as in the case of the previous compound (IV, R = *p*-tolyl). The compound crystallised from glacial acetic acid in yellowish shining rectangular plates, m.p. 177-78°. (Found : N, 11·12. $C_{18}H_{15}O_4N_3S$ requires N, 11·38 per cent).

Reduction of the above Compound (IV, R = *p*-phenetyl): *Formation of 5*-p-*Phenetylaminothiazole-2:3(2′:3′)-quinoline* (V, R = *p*-phenetyl).—The method of procedure was the same as in the case of the previous compound (V, R = *p*-tolyl). The compound crystallised from alcohol in brownish white rectangular plates, m. p. 175°. (Found : N, 13·27. $C_{18}H_{15}ON_3S$ requires N, 13·08 per cent). It is insoluble in alkali and is not desulphurised by yellow oxide of mercury.

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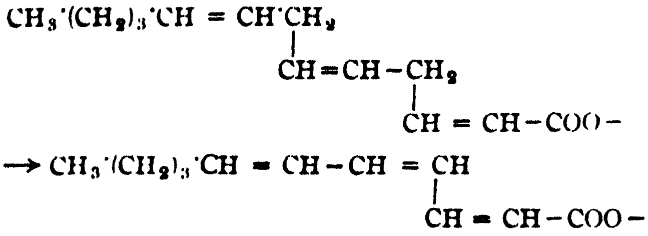
COMPOSITION OF BOILED OIL. A PRELIMINARY NOTE.

BY M. GOSWAMI AND A. SAHA.

In a previous paper on the subject, one of us (*Science and Culture*, 1935, **1**, 183) put forward that the chemical change, when boiled oil is prepared from linseed oil in presence of catalysts like oleates, linoleates or rosinates of manganese, cobalt, lead or nickel, consists in the formation of compounds containing conjugated double bonds ; and in the case of linolenic acid residue there is rearrangement of double bonds to form alternate single and double ones :



$$CH_3{\cdot}(CH_2)_3{\cdot}CH = CH{\cdot}CH_2{-}CH{=}CH{-}CH_2{-}CH = CH{-}COO{-}$$

$$\longrightarrow CH_3{\cdot}(CH_2)_3{\cdot}CH = CH{-}CH = CH{-}CH = CH{-}COO{-}$$

Experiments have now been done to verify this and other views (*loc. cit.*). It has been found that when linseed oil of nil Diene number is boiled in presence of catalysts under the conditions of technical boiling pan with regulated supply of air, the Diene value* gradually increases indicating the formation of compounds containing conjugated double bonds.

Experiments are now being done with finely divided metals to verify other points, *viz.*,

(*i*) In the boiled oil pan it is the finely divided metals which really act as catalysts.

(*ii*) Olein and linolein or the oils containing them in presence of salt catalysts or the corresponding finely divided metals and air form first (*a*) hydroxy compounds then by elimination of H_2O, (*b*) unsaturated compounds and finally, by rearrangements of double bonds, (*c*) compounds containing conjugated double bonds.

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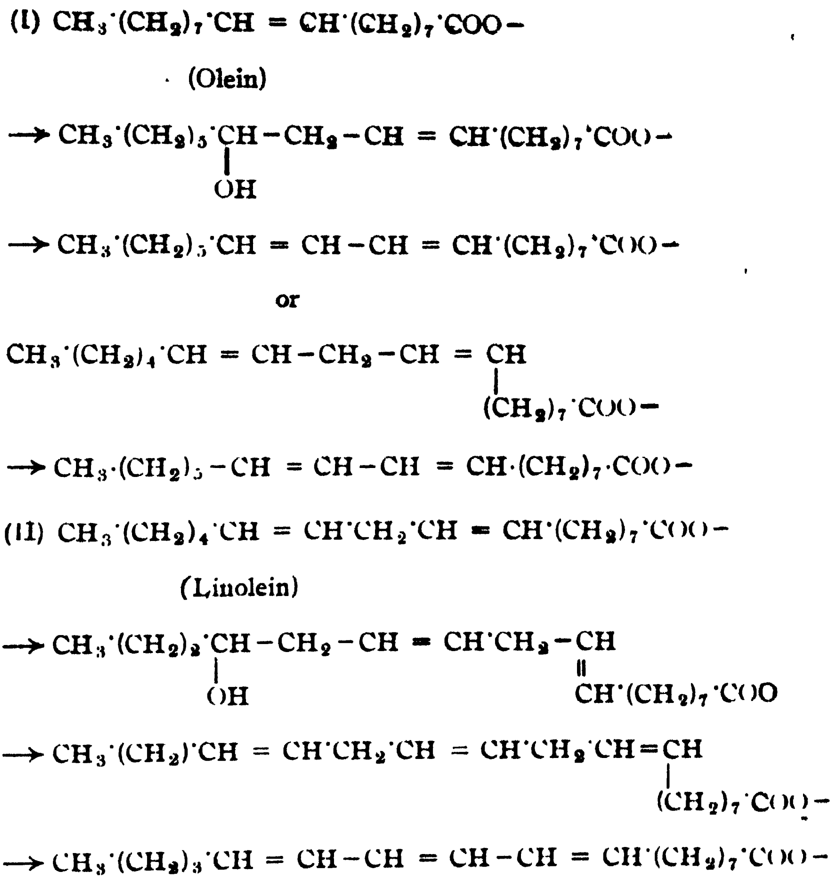
* $\frac{a-b}{c} \times 1{\cdot}269$, where a = no. of c.c. of $N/10$-NaOH required to neutralise 10 c.c. of 1% solution of maleic anhydride heated in a sealed tube in blank experiment ; b = no. of c.c. of $N/10$-NaOH required to neutralise the excess of 10 c.c. of 1% solution of maleic anhydride which remains when oil is heated with it in a sealed tube ; e = weight of oil in g. (*vide* Kaufmann and Baltes, *Fette u. Seifen*, 1936, **43**, 93)

(*iii*) Linolein or oils containing it under the same conditions may produce directly (*c*) of (*ii*).

The changes of (*ii*) and (*iii*) may be represented thus :



(I) $CH_3\cdot(CH_2)_7\cdot CH = CH\cdot(CH_2)_7\cdot COO-$

(Olein)

$$\rightarrow CH_3\cdot(CH_2)_5\cdot\underset{OH}{\underset{|}{C}}H-CH_2-CH = CH\cdot(CH_2)_7\cdot COO-$$

$$\rightarrow CH_3\cdot(CH_2)_5\cdot CH = CH-CH = CH\cdot(CH_2)_7\cdot COO-$$

or

$$CH_3\cdot(CH_2)_4\cdot CH = CH-CH_2-CH = \underset{(CH_2)_7\cdot COO-}{\underset{|}{CH}}$$

$$\rightarrow CH_3\cdot(CH_2)_5-CH = CH-CH = CH\cdot(CH_2)_7\cdot COO-$$

(II) $CH_3\cdot(CH_2)_4\cdot CH = CH\cdot CH_2\cdot CH = CH\cdot(CH_2)_7\cdot COO-$

(Linolein)

$$\rightarrow CH_3\cdot(CH_2)_3\cdot\underset{OH}{\underset{|}{C}}H-CH_2-CH = CH\cdot CH_2-\underset{CH\cdot(CH_2)_7\cdot COO}{\underset{\|}{CH}}$$

$$\rightarrow CH_3\cdot(CH_2)\cdot CH = CH\cdot CH_2\cdot CH = CH\cdot CH_2\cdot CH=\underset{(CH_2)_7\cdot COO-}{\underset{|}{CH}}$$

$$\rightarrow CH_3\cdot(CH_2)_3\cdot CH = CH-CH = CH-CH = CH\cdot(CH_2)_7\cdot COO-$$

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A NOTE ON THE APPLICATION OF POTASSIUM FERRICYANIDE METHOD FOR THE ESTIMATION OF REDUCING SUGARS IN CANE JUICE.

By Sailesh Chandra Sen.

The estimation of glucose (reducing sugar) is generally made by Fehling's method. Attempts have, however, been made to estimate glucose in cane juice by Cole's (*Biochem. J.*, 1933, 27, 723) 1% potassium ferricyanide method with slight modification and excellent comparative results with the Fehling's solution have been obtained with the clear sodium phosphate filtrate of cane juice.

EXPERIMENTAL.

To a cold solution of potassium ferricyanide (1%, 20 or 40 c.c.), caustic potash (5 %, 5 or 10 c.c.) containing a drop of 1 % methylene blue in a conical flask (200 c.c.) about half the volume of sugar solution to be titrated were added and the solution heated to boiling on a wire gauze over a flame. The flame was then lowered and the sugar solution added allowing a few seconds between each addition until the fluid was decolourised within 32 seconds after one shake in case of exact titration. With an excess of sugar solution it takes more time for the after-blueing to occur. The whole operation should be completed within 2-3 minutes.

Comparison of the standard solutions with 1% dextrose and lævulose (3 %) is given in Tables I and II.

TABLE I.

Standard solution.	Dextrose (B. P., 1%) reqd. for titration.	Lævulose (B. P. 1 %) reqd. for titration.	Remarks.
Potassium ferricyanide solution (1 %, 20 c.c.)	2 c.c.	2 c.c.	The mean result of 10
Fehling's solution (4 c.c.)	2 c.c.	2 c.c.	Readings tabulated

TABLE II.

Serial Nos.	Standard solution.	Cane juice reqd. for titration.	Vol. of lead sub-acetate filtrate reqd. for titration.	Vol of sodium phosphate filtrate reqd. for titration
1*	20 c.c. 1 % ferricyanide solution	2·70 c c.	3·2 c.c.	3·20 c c.
	4 c.c. Fehling's	3·20	...	3·20
2	20 c.c. Ferricyanide	3·70	3·7	3·80
	4 c.c. Fehling's	3·20	...	3·85

The estimation of reducing sugars with Fehling's as well as with ferricyanide solution has been carried out with over two hundred of cane juice samples for the last two years. The results in the case of the sodium phosphate filtrate compared very well with these two standard solutions. With ferricyanide solution, a difference of values in the cane juice and the sodium phosphate filtrate is often observed. For the comparison of the results, two standard solutions of equivalent strength were always taken.

My thanks are due to Mr. J. N. Mukherjee, the Imperial Agricultural Chemist for his kind help in giving me the facilities for carrying out this work.

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* The mean result of 6 readings.

A NOTE ON THE USE OF ADSORPTION INDICATOR IN ACIDIMETRY AND ALKALIMETRY.

BY SACHINDRA NATH ROY.

In a previous communication (Roy, *J. Indian chem. Soc.* 1936, **18**, 436) the applicability of adsorption indicators in acidimetry and alkalimetry has been described where fluorescein was used as the adsorption indicator in conjunction with lead nitrate. In the present paper attempts have been made to describe the use of fluorescein as an adsorption indicator in conjunction with stannous chloride.

A known volume of standard hydrochloric or sulphuric acid (strength not less than *N*/15) was taken in a conical flask to which a few drops of fluorescein (0·5% solution of sodium fluoresceinate) and traces of stannous chloride were added and the mixture titrated with caustic soda or sodium carbonate. The end-point was marked by the sudden disappearance of the dull-green colour of the solution and consequent development of a distinct yellowish red colour. The solution becomes turbid at the same time. Eosin may be used instead of fluorescein in which case the colour changes from a dull red to a brilliant turbid violet.

The strengths of the alkali and the acid determined in this way were compared with those obtained by titration with methyl orange as indicator and two results were found to be concordant in moderate dilution, as will be evident from the following table.

Conc. of acid or alkali (approx.)	Vol. of alkaline soln. required for a known vol. of acid.	Vol of alkaline soln for the same vol. of acid.
·	(Methyl orange)	($SnCl_2$ & fluorescein or eosin)
N/2	15·40	15·40
N/5	15·50	15·50
N/8	15·45	15·45
N/10	18·50	18·55
N/15	18·50	18·60

The best results were obtained with $N/2$ to $N/10$ solution. In dilute solutions the results slightly differ from those obtained by using methyl orange. This is due to the fact that stannous chloride gives a weak acid reaction in solution and hence a larger volume of alkali will be necessary to effect the desired colour change. For the same reason acetic acid can not be determined accurately by this method. Large neutral salts effect the colour change to a considerable degree.

The mechanism of the reaction may be explained in the following way,—when all the acid is neutralised, the excess drop of alkali hydoxide or carbonate reacts with stannous chloride forming stannous hydroxide, on which are adsorbed stannous and fluorescein ions from the solution with the development of a pink colour on the surface of the precipitate.

My thanks are due to Prof. A. Maitra for his kind interest in the work.

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REVIEWS

Liesegang Rings and the Influence of Media on Their Formation.

By A. C. Chatterji, D.Sc., Dr. Ing. (Newul Kishore Press, 1936.)

This is one of the series of publications from the Lucknow University edited by Professor B. Sahni, Sc.D., F.R.S. After a short general introduction, the author has described a series of experimental results where the influence of the nature of the gel on the formation of periodic precipitates of lead chloride, lead iodide and silver molybdate has been recorded. These results have been discussed in the light of the peptising influence of gel materials and have been shown to be in accordance with the explanation of the Liesegang phenomenon advanced by N. R. Dhar and the author. The adsorption theory of Bradford and the supersaturation theory first suggested by W. Ostwald have been discussed and are considered inadequate. In the short space of 29 pages the reader is presented with an excellent critical summary of the author's and Dhar's theory of the Liesegang phenomenon.

A short bibliography is included. One misses, however, in the body of the book, reference to a recent publication on the subject by E. S. Hedges (Liesegang rings. Chapman and Hall, 1932) where a critical analysis of the author's theory is also given. In the references to literature in the pamphlet the names of Journals have unfortunately been left out.

P. B. G.

Annual Tables of Constants and Numerical Data-Radioactivity, Nuclear Physics, Transmutations, Neutrons, Positrons.

Years 1931 to April 1936—Reprint from Vol. XI Edited by I. Joliot-Curie, B. Grinbey, R. J. Walen.

These well known ATC volumes are published usually annually and contain a well sifted summary of the physical and chemical constants and numerical data which have appeared in print within a certain period. Those bearing on a special subject can now be obtained in the form of reprints. The present one contains the data on radioactivity and other allied subjects covering the period 1931—April 1936, and the name of Mme. Irene Joliot-Curie amongst the editors, is a guarantee of the reliability of the data collected.

The volume is divided into two parts. Part (A) deals with natural radioactivity and contains chapters on half-periods, α-, β- and γ rays, radioactivity of potassium and of the rare earths, calorimetry and chemical effects of radiations.

Part (B) deals with transmutations, artificial radioactivity, protons, stable isotopes, neutrons and positrons. This part contains, so far as is known to the reviewer, the first systematic and detailed summary of the whole of the experimental data on the newly created subject of transmutations and artificial radioactivity, and will prove extremely useful to all workers in these subjects.

D. M. B

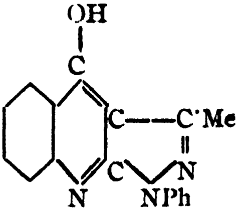
QUINOLINE DERIVATIVES. PART II.

By Tejendra Nath Ghosh.

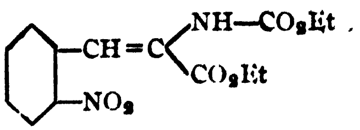
Antipyrine, discovered by Knorr in 1887, has greater antipyretic activity than quinine, but has no specific action against malaria. It was, therefore, thought that, if a quinoline derivative with fused pyrazolone ring could be synthesised, such a compound will have antipyretic activity and, at the same time, is expected to possess antimalarial properties, due to the presence of the quinoline residue.

Knorr and Jödicke (*Ber.*, 1885, **18**, 2262) obtained a pyrazolinoquinoline by reducing the product obtained from *o*-nitrobenzoylacetoacetic ester and phenylhydrazine. Narang, Rây and Singh (*J. Indian Chem. Soc.*, 1934, **11**, 427) synthesised a pyrazolinoquinoline derivative, the pharmacological examination of which is still under investigation.

It has been thought worth while to explore other new methods for the synthesis of pyrazolinoquinolines. With this object in view, 1-phenyl-3-methylpyrazolone has been condensed with anthranilic acid at 130-140° in presence of fused sodium acetate, when the pyrazolinoquinoline derivative (I) is obtained with the elimination of two molecules of water,



(I)

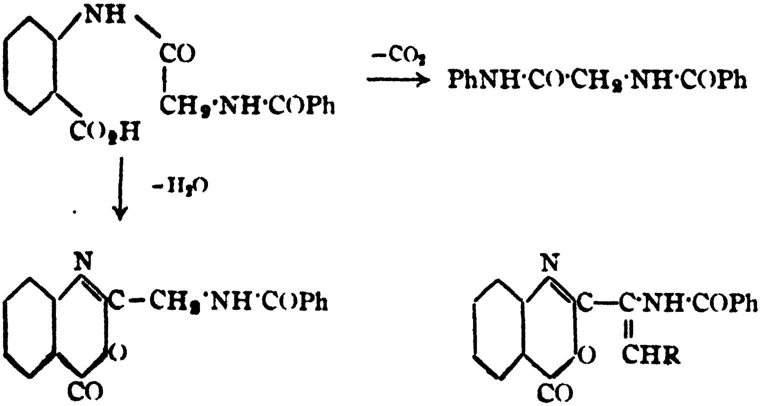


(II)

Although 6-aminoquinoline and 8-aminoquinoline have no action on paramaecia in strength of 1 : 4000, the introduction of OH-group into these quinoline derivatives raises their toxic action on paramaecia to a remarkable degree (Brahmachari, *et al.*, *J. Pharm. Expt. Therap.*, 1931, **41**, 255 ; 1932, **44**, 445). With this idea in view, an investigation was started for the synthesis of some aminohydroxyquinoline derivatives, so that their antimalarial action can be studied. Urethanylacetic ester has now been condensed with *o*-nitrobenzaldehyde in presence of acetic anhydride and fused sodium acetate, when a-urethanyl-*o*-nitrocinnamic ester (II) is obtained. The compound (II) on reduction was expected to give α-hydroxy-β-carbethoxyaminoquinoline and subsequent hydrolysis would give 2-hydroxy-3-aminoquinoline.

Reduction of the compound (II) with zinc dust and acetic acid did not proceed smoothly. An impure product was obtained, which, however, could not be crystallised. With tin and hydrochloric acid, the compound yields the hydrochloride of *o*-aminocinnamic acid with the disruption of the urethanyl group.

With a view to synthesise αγ-diketo-β-aminobenzoyltetrahydroquinoline, hippuric acid has now been condensed with anthranilic acid at 145-150° in presence of fused sodium acetate, when a mixture of the anilide of hippuric acid and a compound possessing the composition $C_{16}H_{12}O_3N_2$ is obtained. That the latter compound possesses the structure (III) is proved by the fact that it contains a reactive methylene group and condenses with aldehyde to give the compound (IV).



(III) (IV)

EXPERIMENTAL.

Condensation of 1-Phenyl-3-methylpyrazolone with Anthranilic Acid: Formation of 1-Phenyl-3-methylpyrazoline-4:5 (2':3')-4'-hydroxyquinoline (I).—An intimate mixture of 1-phenyl-3-methylpyrazolone (8·7 g.) and anthranilic acid (6·8 g.) was fused at 130-140° and finely powdered fused sodium acetate (6 g.) was slowly added during 1 hour. The mass was heated at 130-140° for 4 hours. On cooling, it was treated with aqueous sodium bicarbonate solution. The filtered mass was next treated with cold dilute alkali, a small portion remaining undissolved. The alkaline solution, on acidification with excess of hydrochloric acid, yielded a reddish brown pasty mass which was triturated with alcohol. The alcoholic solution left a precipitate free from pasty matter, which crystallised from large quantity of alcohol in slender yellowish needles, m.p. 175-76°, yield 1 g. (Found: C, 73·82; H, 5·11; N, 15·48. $C_{17}H_{13}ON_3$ requires C, 74·18; H, 4·72; N, 15·27 per cent). When boiled with strong hydrochloric acid or with a mixture of strong hydrochloric acid and glacial acetic acid, it remains unchanged. This shows that the compound, under these conditions, does not form a hydrochloride and, in this respect, resembles the compound of Knorr and Jödicke (*loc. cit.*). It is insolubie in aqueous bicarbonate but soluble in dilute alkali and precipitated by acids. It gives a dark brown colouration with ferric chloride.

The alkali-insoluble product crystallised from alcohol in light yellow needles, m. p. 142-43°. (Found: N, 11·97, 11·81). When boiled with strong hydrochloric acid for about 1 hour, it yields a hydrochloride (colourless stout needles), m.p. 95-96°. Further studies of the compound were not possible due to its extremely poor yield.

a-Urethanyl-o-nitrocinnamic Ester (II).—An acetic anhydride solution of urethanylacetic ester (8·8 g., b.p. 161°/90 mm.), *o*-nitrobenzaldehyde (7·6 g.) and fused sodium acetate (5 g.) was heated under reflux for about 4 hours. On cooling and standing overnight, the deep red solution deposited a crystalline product, which was filtered, washed several times with alcohol and water, and finally crystallised from alcohol in brown rectangular plates, m.p. 227-28°, yield 5 g. (Found: N, 8·84. $C_{14}H_{16}O_6N_2$ requires N, 9·09 per cent).

Reduction of the above compound (II): *Formation of o-Amino-cinnamic Acid.*—The above compound (II, 4 g.) was mixed with strong hydrochloric acid and granulated tin, when the reaction commenced with evolution of heat. The mixture was allowed to stand for about 20 minutes and then heated uuder reflux for about 30 minutes, when a dark brown clear solution was obtained. The solution was diluted with water and tin completely removed by passing sulphuretted hydrogen. After filtration, the clear solution was evaporated to a small bulk when a crystalline product was obtained It crystallised from water in colourless shining plates, m p. 186-87° (decomp.), yield 0·5 g. (Found: N, 6·86. $C_9H_9O_2N,HCl$ requires N, 7·03 per cent).

The *free base* was obtained by adding sodium acetate to an aqueous solution of the above hydrochloride. The solid, thus obtained, crystallised from hot water in light yellow needles, m.p. 151-52° (decomp.) and its identity with *o*-aminocinnamic acid was confirmed by studying its properties and finally by analysis.

Condensation of Hippuric Acid with Anthranilic Acid: Formation of Anilide of Hippuric Acid and 1-Keto-3-benzoylaminomethyl-5:6-benzo-2:4-

oxazine (III).—An intimate mixture of hippuric acid (9 g.) and anthranilic acid (6·9 g.) was fused at 165-170° and the molten mass, mixed with finely powdered sodium acetate (6 g.), was heated at 145-150° for about 4 hours. On cooling, the fused mass was treated with aqueous sodium bicarbonate solution. The insoluble portion, the anilide of hippuric acid, was washed several times with water and was finally crystallised from alcohol in colourless plates, m.p. 207-208°, yield 4 g. (Found: N, 10·74. Calc. for $C_{15}H_{14}O_2N_2$: N, 11·02 per cent). Curtius (*J. pr. Chem.*, 1895, *ii*, **52**, 257) obtained this compound (m.p. 208·5°) by the action of aniline on hippurazide. When it is heated with strong hydrochloric acid for about an hour, the solution yields on cooling and dilution with water a crystalline solid which is identified to be hippuric acid.

The bicarbonate solution, on acidification with excess of hydrochloric acid, yielded a solid which proved to be a mixture of the compound (III) and unreacted hippuric acid, from which the latter was removed by treating the solid several times with boiling water. The compound (III), which is sparingly soluble in hot water, was crystallised twice from alcohol in colourless slender needles, m.p. 205-207°, yield 2 g. [Found: N, 10·11. M.W (by titration with baryta), 282. $C_{16}H_{12}O_3N_2$ requires N, 10·0 per cent. M. W., 280]. When this compound is boiled for nearly 3 hours with strong hydrochloric acid, the solution on cooling and dilution with water, yields a solid identified to be hippuric acid. The mother-liquor, shaken several times with ether, yielded, on evaporation a crystalline solid identified to be anthranilic acid hydrochloride.

Condensation of the Compound (III) *with* o-*Nitrobenzaldehyde: Formation of* (IV, $R = C_6H_4 \cdot NO_2$).—An acetic anhydride solution of equimolecular proportions of the compound (III) and *o*-nitrobenzaldehyde was heated under reflux in presence of fused sodium acetate for nearly 3 hours. On cooling the solution was treated with excess of aqueous sodium carbonate solution. The carbonate solution was filtered and acidified with dilute hydrochloric acid, when a solid was obtained which crystallised from alcohol in brownish rectangular plates. It melts at 234-35° to a viscous red liquid. (Found : N, 10·04. $C_{23}H_{15}O_5N_3$ requires N, 10·17 per cent).

My thanks are due to Prof. P. C. Guha for his kind interest in this investigation. My thanks are also due to the Lady Tata Memorial Trust for the award of a scholarship.

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SPIRO-COMPOUNDS. PART III. SYNTHESIS OF *CYCLO* HEXANE-SPIRO-*CYCLO*BUTANE DERIVATIVES BY THE APPLICATION OF THE DIECKMANN REACTION TO ESTERS OF THE TRICARBALLYLIC SERIES.

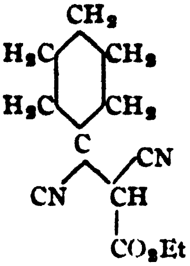
By Nripendra Nath Chatterjee.

On the basis of the Baeyer's strain theory, the *cyclo*butane ring should be formed much more easily than the *cyclo*propane ring, and less easily than the *cyclo*hexane and *cyclo*pentane rings, but the methods which are used for the synthesis of three , five- and six-membered rings break down wholly or partially in the case of the four-membred ring. The thermochemical data of Stohmann and Kleber (*J. pr. Chem.*, 1892, *ii*, **45**, 475) are also at variance with the strain theory. This anomaly has been explained by Ingold (*J. Chem. Soc.*, 1921, **199**, 305) by assuming that the angle between the two carbon valencies *via* polymethylene chain is 115·2° and not 109·5° as assumed by Baeyer.

The effect of *gem*-dialkyl grouping in promoting ring formation is evident from the work of Perkin and Thorpe (*J. Chem. Soc.*, 1904, **85**, 138), Kon (*J. Chem. Soc.*, 1921, **119**, 810; 1922, **121**, 513) and this has been explained on the valency deflection theory by Thorpe, Ingold and others (*J. Chem. Soc.*, 1915, **107**, 1080).

The effect of *cyclo*hexane, methyl*cyclo*hexane, *cyclo*pentane and *gem*-dialkyl grouping, attached to a tricarballylic acid residue, on the formation and stability of a spiro-*cyclo*butane ring has been studied and it has been observed that *cyclo*butane derivative could only be isolated in the case when it is combined with a *cyclo*hexane ring. Freshly distilled *cyclo*hexanone cyanohydrin is condensed with the sodium salt of ethyl cyanoacetate (*cf.* Dickens, Horton and Thorpe, *J. Chem. Soc.*, 1924, **125**, 1830) and the sodium salt of ethyl 1-cyano*cyclo*hexane-1-cyanoacetate (I), thus obtained, is allowed to react with ethyl bromoacetate to yield diethyl 1-cyano*cyclo*hexane-1-cyanosuccinate (II). On hydrolysis the above ester yields 1-carboxy*cyclo*hexane-1-succinic acid (III). The corresponding ester yields diethyl *cyclo*hexane-spiro-*cyclo*butane-2-one-3:4-dicarboxylate (IV) when heated with sodium in xylene. The yield of the keto-ester is very poor, barely reaching 1%

of the theoretical. This ester in alcoholic solution gives a reddish violet colouration with ferric chloride and when oxidised by means of nitric acid yields *cyclo*hexane-1 : 1-dicarboxylic acid. Further corroborative proof is being collected in support of spiro-*cyclo*butanone structure.



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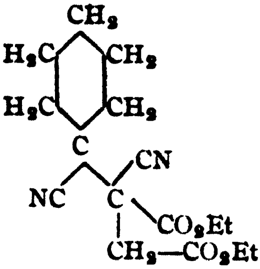

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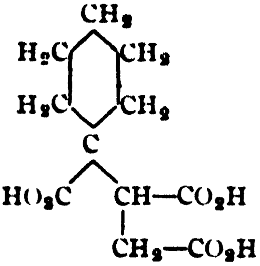

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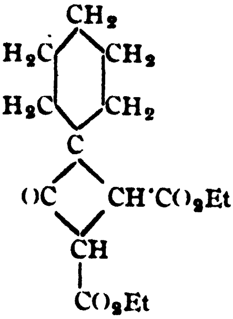

(IV)

The products obtained from other ketone-cyanohydrins are tabulated below.

Cyanohydrins.	Condensation products.	Products after hydrolysis.	Esters of the tribasic acids.
4-Methyl*cyclo*hexanone-cyanohydrin	Diethyl 4-methyl-1-cyano-*cyclo*hexane-1-cyanosuccinate	4-Methl*cyclo*hexane-1-carboxylic-1-succinic acid (A)	Triethyl 4-methyl-*cyclo*hexane-1-carboxylate-1-succinate
2-Methyl*cyclo*hexanone-cyanohydrin	Diethyl 2-methyl-1-cyano-*cyclo*hexane-1-cyanosuccinate	2-Methyl*cyclo*hexane-1-carboxylic-1-succinic acid (B)	Triethyl 2-methyl*cyclo* hexane-1-carboxylate-1-succinate

Cyanohydrins.	Condensation products.	Products after hydrolysis.	Esters of the tribasic acids.
*cyclo*Pentanone-cyanohydrin	Diethyl 1-cyano*cyclo*pentane-1-cyanosuccinate	*cyclo*Pentane-1-carboxylic-1-succinic acid	Triethyl *cyclo*pentane-1-carboxylate-1-succinate (C)
Acetone-cyanohydrin	Diethyl 2-methyl-2:3-dicyanobutane-3:4-dicarboxylate	$\alpha\alpha$-Dimethyltricarballylic acid (F)	Triethyl $\alpha\alpha$-dimethyltricarballylate (D)
3-Methyl*cyclo*hexanone-cyanohydrin	Diethyl 3-methyl-1-cyano-*cyclo*hexane-1-cyanosuccinate	3-Methyl*cyclo*hexane-1-carboxylic-1-succinic acid (E)	Triethyl 3-methyl*cyclo*hexane-1-carboxylate-1-succinate

Triethyl 4-methyl-*cyclo*hexane-1-carboxylate-1-succinate undergoes ring closure in presence of sodium in xylene to yield 4′-methyl*cyclo*hexane-spiro-*cyclo*butane-2-one-3:4-dicarboxylate. In alcoholic solution it gives a reddish violet colouration with ferric chloride.

Attempt has also been made with the esters (C and D) to effect the ring-closure but no definite product could be isolated.

The acid (F) is known as the oxidation product of many terpene compounds (Tiemann and Semmler, *Ber.*, 1895, **28**, 1349; Gardner and Cockburn, *J. Chem. Soc.*, 1898, **73**, 708: Jagelki, *Ber.*, 1899, **32**, 1509; Baeyer, *ibid.*, 1896, **29**, 2792). The synthetic method of preparing this acid is that due to Haller and Blank (*Compt. rend.*, 1900, **131**, 19) who obtained it by hydrolysing the condensation product of ethyl cyanosuccinate and ethyl α-bromo*iso*butyrate (Barthe, *Compt. rend.*, 1897, **125**, 182) by means of hydrochloric acid. Other synthetic methods are those due to Bome and Spränkling (*J. Chem. Soc.*, 1902, **81**, 49) and Clemo and Welch (*J. Chem. Soc.*, 1928, 2621).

Compounds (A, B and E) may occur in two or more forms. Experiments are in progress to separate them.

EXPERIMENTAL.

*Diethyl 1-cyano*cyclo*hexane-1-cyanosuccinate.*—To a well-cooled solution of freshly distilled *cyclo*hexanone-cyanohydrin (186 g.) in absolute alcohol (186 c.c.), a suspension of ethyl sodiocyanoacetate, obtained from ethyl cyanoacetate (168 g.), sodium (33 g.) and alcohol (500 c.c.), was gradually added with vigorous shaking. The mixture after being kept in ice for 6 hours and at room temperature for 3 days was mixed with ethyl bromoacetate (280 g.) and after the initial reaction had abated was boiled under reflux until it was neutral to litmus (8 hours). The mixture was filtered and the filtrate diluted with water and extracted with ether, the ethereal solution washed with water, dried and the ether removed. It distilled as a viscous liquid, b.p. 200-205°/7 mm , yield 170 g. (Found : C, 62·6; H, 7·2 $C_{16}H_{22}O_4N_2$ requires C, 62·7; H, 7·19 per cent).

*1-Carboxy*cyclo*hexane-1-succinic Acid.*—The foregoing ester (20 g) was mixed with sulphuric acid (70 %, 120 c c.) and boiled under reflux for 12 hours. The condenser was removed from time to time to allow the alcohol formed to escape. The solution was then diluted with water and extracted with ether, and the ethereal solution was treated with sodium carbonate. On acidification of the carbonate solution a product was obtained which was heated on the water-bath with a solution of caustic alkali (15 %) for 3-4 hours The alkaline solution was then acidified and extracted with ether. After removing ether the product was kept in a desiccator when it solidified. It crystallised from ether, m. p. 187° (decomp.), yield 10 g. (Found : C, 54·7; H, 6·5. $C_{11}H_{16}O_6$ requires C, 54·1; H, 6·5 per cent).

Triethyl cyclo*hexane-1-carboxylate-1-succinate* was obtained in an almost quantitative yield from the acid by the alcohol vapour method. In a typical experiment the acid (20 g.), absolute alcohol (60 c.c.), concentrated sulphuric acid (6 c.c.), 3 litres of vaporised alcohol (3-4 hours) gave 22 g. of the ester, b.p. 174-76°/6 mm. (Found : C, 62·1; H, 8·4. $C_{17}H_{28}O_6$ requires C, 62·1; H, 8·5 per cent).

Diethyl cyclo*hexane-spiro*-cyclo*butane-2-one-3:4-dicarboxylate* (IV).—A mixture of the foregoing ester (30 g.) and granulated sodium (4·3 g.) in dry xylene (150 c.c.) was heated on an oil-bath at about 150° for ¾ hour. The sodium gradually dissolved and a red jelly filled the flask. Frequent shaking was necessary to prevent local overheating, leading to decomposition, and 50 c.c. of xylene after 20-30 minutes were added to prevent the mass from becoming too solid. When cooled the reaction mixture was decomposed with ice and ice-cold dilute sulphuric acid. The products of six such operations were combined. The acid aqueous layer was separated from the xylene solution and extracted with ether, which was added to the xylene solution. After washing with water this solution was treated with sodium carbonate solution. After washing with water and drying over sodium sulphate, the ether-xylene solution was fractionated. The ester was obtained as a pale yellow oil, b p. 178-80°/6 mm. (Found : C, 63·1; H, 7·4. $C_{15}H_{22}O_5$ requires C, 63·8; H, 7·8 per cent).

Oxidation of cyclo*Hexane-spiro-*cyclo*butane-2-one-3:4-dicarboxylate.*— The keto-ester (1 5 g.) was warmed with an excess of concentrated nitric acid until most of the red fumes disappeared. The resulting solution was then boiled for a few minutes and finally evaporated to dryness. The residue was treated with water and again evaporated ; the semi-solid mass, thus obtained, was left on a porous plate and after crystallisation from water the *cyclo*hexane-1:1-dicarboxylic acid melted at 176° (decomp.) (*lit.* m. p 176°).

Almost identical conditions were employed in the preparation of the compounds described in the following table.

	Products.	B.p. or M.p.	Formula.	Analysis. Found.	Calc.	Yield.
(1) 4-Methyl-*cyclo*hexanone cyanohydrin (190 g.)	Diethyl 4-methyl *cyclo*hexane-1-cyano-1-cyanosuccinate	203°-210°/6 mm. m p. 90° cryst. from ether	$C_{17}H_{24}O_4N_2$	C, 64·1, H, 7·5 N, 8·8	63·7 ; 7·5 8·75	150 g.
Product of hydrolysis (20 g. of cyanoester)	4-Methyl-*cyclo*hexane-1-carboxylic-1-succinic acid	m.p. 188° cryst. from ether	$C_{12}H_{18}O_6$	C, 56·5 H, 7·0	55·8 6·9	12 g.
Ester	Triethyl 4-methyl-*cyclo*hexane-1-carboxylate-1-succinate	178°-80°/5 mm.	$C_{18}H_{30}O_6$	63·0 8·7	63·1 8·7	Quantitative
Dieckmann reaction product	4′-Methyl *cyclo*hexane-spiro-*cyclo*butane-2-one-3 :4-dicarboxylate	177°-85° 5 mm.	$C_{16}H_{24}O_5$	64·1 8·4	64·8 8·1	About 1 per cent.
(2) 2-Methyl*cyclo*hexanone cyanohydrin (180 g.)	Diethyl 2-methyl *cyclo*hexane-1-cyano-1-cyanosuccinate	200°-208°/6 mm.	$C_{17}H_{24}O_4N_2$	64·0 7·6	63·7 7·5	50 g.
Product of hydrolysis (20 g. of cyanoester)	2-Methyl-*cyclo*hexane-1-carboxylic-1-succinic acid	No definite isomer could be isolated	$C_{12}H_{18}O_6$	56·4 7·2	55·8 6·9	10 g.
Ester	Triethyl-2-methyl-*cyclo*hexane 1-carboxylate-1-succinate	175°-76°/4 mm.	$C_{18}H_{30}O_6$	63·3 8·7	63·1 8·7	Quantitative

	Products.	B.p. or M.p.	Formula.	Analysis.		Yield.
				Found.	Calc.	
(3) 3-Methyl*cyclo*hexanone cyanohydrin (180 g.)	Diethyl 3-methyl *cyclo*hexane-1-cyano-1-cyanosuccinate	200-205°/6 mm.	$C_{17}H_{24}O_4N_2$	C, 64·0 H, 7·7	63·7 7·5	120 g.
Product of hydrolysis (20 g. of cyano ester)	3-Methyl-*cyclo*hexane-1-carboxylic-1-succinic acid	No definite isomer could be isolated	$C_{12}H_{18}O_6$	56·5 7·3	55·8 6·9	10 g.
Ester	Triethyl 3-methyl-*cyclo*hexane-1-carboxylate-1-succinate	178°/5 mm.	$C_{18}H_{30}O_6$	63·4 8·6	63·1 8·7	Quantitative
(4) *cyclo*Pentanone cyanohydrin (186 g.)	Diethyl *cyclo*pentane 1-cyano-1-cyanosuccinate	197°-203°/7 mm	$C_{15}H_{20}O_4N_2$	62·0 6·9	61·6 6·8	120 g.
Product of hydrolysis (20 g. of cyano-ester)	*cyclo*Pentane-1-carboxylic-1-succinic acid	m.p 159° cryst. from ether	$C_{10}H_{14}O_6$	52·75 6·1	52·15 6·08	11 g.
Ester	Triethyl *cyclo*pentane-1-carboxylate 1-succinate	173°-75°/7 mm.	$C_{16}H_{26}O_6$	61·1 8·1	61·1 8·2	Quantitative
(5) Acetone cyanohydrin (90 g.)	Diethyl 2-methyl-2 .3-dicyanobutane-3 :4-dicarboxylate	180°-82° 6 mm.	$C_{13}H_{18}O_4N_2$	58·7 6·6	58·6 6·7	50 g.
Product of hydrolysis (20 g. of cyano-ester)	αα-Dimethyltricarballylic acid	m p 186° cryst. from dilute HCl	$C_8H_{12}O_6$	46·8 5·8	47·06 5·8	8 g.
Ester	Triethyl αα-dimethyltricarballylate	160° 5 mm	$C_{14}H_{24}O_6$	58·3 8·5	58·3 8·3	Quantitative

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ON THE NATURE OF THE ELECTRIC CHARGE OF A PRECIPITATE FORMED IN PRESENCE OF AN EXCESS OF EITHER OF ITS CONSTITUENT IONS.

PART I.

By Subodh Gobinda Chaudhury and Jyotirmoy Sen-Gupta.

In a previous paper (*J. Indian Chem. Soc.*, 1936, **13**, 670) it has been shown that the nature of the electric charge of a ferrocyanide precipitate, formed from the precipitants, when they are equivalent or one in excess of another, shows that when the concentration of the electrolytes taken is 0·1*N*, the charge of copper and uranium ferrocyanide is always positive, while that of zinc ferrocyanide is negative but when the concentration is 0·01*N*, the charge of copper ferrocyanide is always negative. From this it would appear that the nature of the charge of a precipitate depends on

(*i*) the nature of the electrolytes taken for precipitation of a particular precipitate and also on, (*ii*) the concentrations of the electrolytes taken and (*iii*) is independent of the sequence of mixing, *i.e.*, whether an electrolyte MN is added to another PQ or the latter added to the former.

These results are apparently not in agreement with the observations of Lotter Moser on silver halides (*J. pr. Chem.*, 1905, *ii*, **72**, 39; Lotter Moser and Lothe, *Z. physikal. Chem.*, 1908, **62**, 359), of Fajans (*ibid.*, 1921, **27**, 478) and of Mukherjee and his co-workers on silver iodide and other systems (*J. Indian Chem. Soc.*, 1926, **3**, 335; 1924, **1**, 173) who found that a slight excess of one of the precipitating electrolytes imparts a charge to the precipitate (silver halide) similar to that of the ion, common to the precipitate and one of the electrolytes taken for precipitation.

Recently however Verwey (*Chem. Rev.*, 1935, **16**, 363) has reported the work of Julien in which it has been shown that silver halides do not always acquire the same charge as that of the constituent ion present in excess. Moreover, in our work (*loc. cit.*) it has been shown that the nature of the charge appears to depend on the initial concentrations and the nature of the electrolytes taken for precipitation. This difference as has been pointed out before (*loc. cit.*), is due to a difference in the nature and the method of preparation of the precipitates to start with. In our experiments, the measurements of cataphoretic velocity were done just at and after the time of precipitation, while in the experiments done by other authors, the starting material was pure, *i.e.*, free from electrolytes. Hence it was thought desirable to re-investigate the nature of the charge in the case of these and other precipitates under different conditions.

EXPERIMENTAL.

Since the point, raised above is cleared up if the nature of the electric charge acquired by the precipitate is known, only the sign of the charge of different precipitates has been measured by the micro-cataphoretic method (*cf.* Mukherjee, Chaudhury and Bhabak, *J. Indian Chem. Soc.*, 1936, **13**, 370; Mukherjee, Chaudhury and Sen-gupta, *ibid.*, 1936, **13**, 428). The following tables contain the experimental results obtained with different precipitates.

TABLE I.

Copper ferrocyanide.

$CuSO_4$ and $K_4Fe(CN)_6$, 50 c.c. each.

(Former added to latter).				(Latter added to former).			
Excess of	Charge after			Excess of	Charge after		
$K_4Fe(CN)_6$ ($N/10$).	Pptn.	2½ hrs.	20 hrs.	$CuSO_4$ ($N/100$).	Pptn.	3 hrs.	22 hrs.
0 c.c.	+	+	+	0	−	−	−
0·5	+	+	+	0·5	−	−	−
1	+	+	− (feeble)	1	− (feeble)	−	−
2	+	+ (feeble)	−	2	0	±	+
3	− (feeble)	−	−	3	− (feeble)	+	+
4	−	−	−	5	+	+	+
5	−	−	−				

TABLE II.

Zinc ferrocyanide.

$ZnSO_4$ and $K_4Fe(CN)_6$, 50 c.c. each.

(Latter added to former).			(Latter added to former).		
Excess of $ZnSO_4$	Charge after		Excess of $ZnSO_4$	Charge after	
(N/10).	Pptn.	20 hrs.	(N/100).	Pptn.	48 hr.
0 c. c.	–	–	0 c. c.	–	–
0·5	–	–	5	–	–
1	–	–	10	–	–
3	–	–	12	–	–
5	– (feeble)	–	14	–	–
8	– („)	–	18	–	–
10	– („)	–	25	0	–
12	+ („)	+			
15	+ („)	+			

TABLE III.

Uranium ferrocyanide.

$UO_2(NO_3)_2, 6H_2O$ and $K_4Fe(CN)_6, 3H_2O$, 50 c.c. each.

(Former added to latter).			(Latter added to former).		
Excess of $K_4Fe(CN)_6$	Charge after		Excess of $UO_2(NO_3)_2$	Charge after	
(N/10).	Pptn.	48 hr.	(N/100).	Pptn.	20 hr.
0 c. c.	+	+	0 c. c.	–	–
0·5	+	+	10	–	–
5	+	+	15	–	–
10	+	+	20	–	–
12	0	+	25	–	–
15	+	+	20	–	–
			25	–	– (feeble)
			35	– (feeble)	+ (feeble)

TABLE IV.

Silver Iodide.

$AgNO_3$ and KI, 50 c.c. each

(Latter added to former).			(Latter added to former).		
Excess of $AgNO_3$	Charge after		Excess of $AgNO_3$	Charge after	
(*N*/10).	Pptn.	20 hrs.	(*N*/100).	Pptn.	21 hrs
0 c. c.	–	–	0 c. c.	–	–
0·5	+	–	0·5	+	–
1	+	–	1	+	–
2	+	+	2	+	+
5	+	+			
10	+	+			

TABLE V.

Silver Iodide.

$AgNO_3$ and KI, 50 c.c. each (latter added to former).

Excess of KI (*N*/10)	Charge after precipitation.	Charge after 22 hrs.
0 c. c.	–	–
0·5	–	–
1	–	–
2	–	–

DISCUSSION.

The reaction between copper sulphate and potassium ferrocyanide is represented by

$$2\ CuSO_4 + K_4Fe(CN)_6 = Cu_2Fe(CN)_6 + 2\ K_2SO_4.$$

Here we have the copper ferrocyanide precipitate and in solution potassium sulphate. When the concentrations of the precipitating electrolytes are high (here *N*/10), the initial charge is always positive (even if copper sulphate is added to potassium ferrocyanide, in which case, the chance of the precipitate being negatively charged is greater) when the electrolytes taken for precipitation are equivalent or even when excess of potassium ferrocyanide [0·5 c.c. of $N/10$-$K_4Fe(CN)_6$ in a total volume of 100 c.c.] is taken. With excess of higher and higher concentrations of potassium ferrocyanide, the charge is initially positive but becomes negative with time until at an excess of 3 c.c. of $N/10$-$K_4Fe(CN)_6$, the charge is negative from the very beginning. At this ($N/10$) and higher concentrations of the precipitation electrolytes when mixed in equivalent quantitites the charge of the precipitate is always positive, irrespective of the method of addition (*cf.* Part II, *loc. cit.*).

If, however, the precipitate is formed from dilutions of electrolytes in equivalent quantities (here taken $N/100$), the charge is negative irrespective of the method of addition of the two electrolytes (*cf.* Part II, *loc. cit*). Here the precipitate remains negative even in excess of copper sulphate (1 c.c. of $CuSO_4$ in a total volume of 100 c.c.) but with still higher concentrations of copper sulphate the charge becomes neutral and then positive. At an excess of 2 c.c. ($CuSO_4$, $N/100$), the time effect is apparent (*cf.* Table I). In order to explain these results, it would be necessary to refer briefly to the theories on the origin of the charge of such precipitates. This mechanism of the origin of the charge of the precipitate or of the primary or initial formation of the double layer was first clearly given by Mukherjee (*Trans. Faraday Soc.*, 1921, **16**, 103) and later on slightly modified by Lange (*cf.* Verwey, *loc. cit.*, Lange and Berger, *Z. Elctrochem.*, 1930, **36**, 171).

In a way, there is no fundamental distinction between the two ideas about the formation of the double layer. Mukherjee (*loc. cit.*) starts from the chemical point of view and assumes that due to residual unbalanced chemical affinity on the surface of a precipitate, one of the constituent ions will be adsorbed during the precipitation thus imparting a definite magnitude and sign of the charge on the individual particles in the precipitate. In presence of excess of one of the constituent ions (*i.e.* to say, the ion fitting in the lattice of the crystal), the particular ion should be primarily adsorbed by the precipitate in preference to other ions present in the solution. Due to the charge so acquired, ions of opposite sign will be attracted near the surface. Some of these ions are mobile and free, others are bound, only the latter being effective in diminishing the surface density of charge. Lange assumes that the primary formation of the double layer is due to a difference in the thermodynamic potential of an ion in the lattice and in the solution. In the case of silver halides, he assumes that the metallic ions (*i.e.* silver) would pass from the solid phase to the solution. Since the solubility product of the halide is constant, some of the halide ions must be precipitated from the solution to the solid phase. Thus silver halides in contact with pure water must be negative as is also experimentally found to be ease, and also the precipitate when initially formed should take up more halide ions than silver for the same reason and thus be negatively charged. According to Mukherjee (*loc. cit.*), the precipitate should have the charge of that constituent ion of the precipitate which is present in excess at the time of precipitation, and the electric density of charge of a precipitate *thus should not depend on the concentrations* of the precipitating electrolytes. According to Lange (*loc. cit.*) the charge of the precipitate *should not also depend on the concentrations* of the precipitating electrolytes when they are taken in equivalent quantities. According to both the theories, when a solution of potassium ferrocyanide is added to copper sulphate, the copper ferrocyanide is formed always in an excess of copper sulphate, and therefore the precipitate should be positively charged, whereas in the reverse way of mixture, the charge should be negative. The facts stated above are not in agreement with the conclusions drawn from these theories.

It is true, according to Mukherjee (*loc. cit.*), that the presence of a concentrated solution of K_2SO_4, may make the charge of the copper ferrocyanide positive, and when the precipitate is formed in a more dilute solution, the concentration of K_2SO_4 is low and is thus not sufficient to reverse the negative charge of the precipitate formed. For this, we have to assume that the initial charge of the copper ferrocyanide precipitate is negative under all conditions and subsequent secondary adsorption of potassium ions modifies the charge depending of course on the concentration of potassium ions present at the time of, and after precipitation. According to the theories stated above, the charge of a precipitate is not independent of the method of addition of the precipitating electrolytes, nd cannot therefore be always initially negative. The considerations set forth above are valid only when the precipitating electrolytes are taken in equivalent quantities. If either of the precipitating electrolytes is in excess, then of course, the non-agreement of facts with derivations from these theories is still more apparent. Data on uranium ferrocyanide precipitate (*cf.* Table III), show the same peculiarities as copper ferrocyanide, and support the conclusions drawn above. A precipitate of zinc ferrocyanide shows a negative charge even in a considerable excess of zinc sulphate (*cf.* Table II), a fact which is difficult to reconcile with the postulations of Mukherjee (which have been fruitful in explaining so many facts observed by others, *loc. cit.*) unless of course it is assumed that subsidiary chemical reactions play a part. It follows that zinc ions should have been adsorbed due to residual chemical affinity on the surface of zinc ferrocyanide (here zinc is divalent and ferrocyanide tetravalent) and the charge should have been positive ; from Lange's theory it follows that in presence of moderate amounts of zinc ions in solution, thermodynamic considerations demand that zinc ion should not have been discharged on the surface of the zinc ferrocyanide and the charge should be thus negative. At higher concentrations, there is a probability (rather remote) of the charge being positive as we actually find. But the fact, that the charge of a precipitate depends, at least in some cases, on the concentrations of the precipitants, goes definitely against the theory of thermodynamic potentials of these ions as the cause of the primary formation of double layer.

So is also the case with silver iodide. Here the concentration effect is absent, *i.e.*, whether silver iodide is precipitated from $N/100$-$AgNO_3$ and $N/100$-KI or from $N/10$-$AgNO_3$ and $N/10$-KI, the charge is always negative, when the precipitants are mixed in equivalent quantities. With slight excess of silver nitrate, the charge, though initially positive, becomes negative afterwards with time. With still higher excess of silver nitrate, the charge is always positive. At the time of our investigations we were not aware of the somewhat similar result obtained by Julien (*cf.* Verwey. *loc. cit.*). It is not apparent from that paper whether the precipitates of silver halides were washed free from all electrolytes and then kept in contact with low concentrations of $AgNO_3$ and then the charge of the precipitate measured or the charge of the freshly formed precipitate in contact with potassium nitrate (formed as a result of the reaction) was measured, as we have done. It will appear that the initial positive charge, presumably due to the primary adsorption of silver ions which are present in excess, is modified and becomes negative with time—a fact which again contradicts the fundamental assumptions of the current theories.

Verwey's (*loc. cit.*) elaboration of Lange's idea on the primary formation of double layer, depending on the thermodynamic potentials of the ions adsorbed and a shift of the zero point of the total potential, does not lead us any further, for *the shift of the zero point* does not evidently depend on the concentrations of the *precipitating electrolytes taken.*

It would appear, however, that the initial charge of these precipitates depends in addition to residual chemical affinity of the surface and to some extent the thermodynamic potential of the constituent ions on their crystalline or jelly-like structure. Thus if Mukherjee's theory be elaborated in the sense that in addition to residual chemical affinity of the surface, adsorption of ions also depends on their thermodynamic potentials and on the crystalline structure of the adsorbent, then there might be possible explanations of all the facts observed. These ideas were explicit though not implicitly stated (*cf.* Mukherjee, *loc. cit.*). Thus during the formation of the precipitate, it acquires an initial charge which is gradually modified due to the adsorption of a number of ions from the solution and with time when equilibrium is obtained, the precipitate finally acquires a definite magnitude and sign of the charge depending on the concentration of the particular ions present at and after the time of precipitation on the structure of the adsorbent. No definite picture can be given of such processes (which appear to be characteristic by themselves) unless their crystalline structure is completely known and further experimental work on other systems is available. All that can be said is that, each and every precipitate has its own characteristic properties, which depends *mainly on the history of its preparation*.

SUMMARY.

1. A polar precipitate does not show the same sign of the charge as the constituent ion present in moderate excess at the time of precipitation.

2. There is a time effect on the density of the charge, *i.e.*, the sign of the charge changes with time, sometimes when the precipitants are taken in equivalent quantities and sometimes when one of the precipitant is present in large excess.

3. The sign of the charge appears to depend on the concentrations of the precipitants taken, and independent of the sequence of mixing.

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CHEMICAL EXAMINATION OF THE SEEDS OF *CICHORIUM INTYBUS*, LINN. CONSTITUENTS OF THE OIL FROM THE SEEDS.

By Ram Nath Misra and Sikhibhushan Dutt.

Cichorium Intybus Linn., called *Kasni* in Hindustani, belongs to the natural order *Compositae,* and is a native of the north western parts of India. The seeds are reputed to be tonic, demulcent and cooling and they are used in various forms for bilious vomiting and obstructed menstruations. The use of Kasni by Indian physicians is much the same as that of Taraxacum in Europe (Kirtikar and Basu, "Indian Medicinal Plants," 1918, **I**, p. 728 ; Dymock, "Pharmacographica Indica," **II**, p. 311).

The roots which are used as adulterants for coffee have been chemically examined. Nietzki (*Arch. Pharm.*, **8**, 327) separated from the flowers a crystalline glucoside $C_{32}H_{34}O_{19}$, $4\frac{1}{2}H_2O$. The bland oil contained in the seeds is the subject of the present investigation. No crystalline substances could be isolated from the seeds but the seeds have been found to contain the following :—Oil (4·7%), phlobaphenes (1%), tannins (1%) and reducing sugars.

EXPERIMENTAL.

An authentic specimen of *Cichorium Intybus* seeds was procured from the neighbourhood. A sample when burnt left 13·8% of a greyish white ash, consisting of 17·5% water-soluble and 82·5% water-insoluble inorganic material consisting mainly of potassium, sodium (traces), calcium, aluminium, sulphate, phosphate, chloride, carbonate and silica.

Extraction of the Oil.—2·5 Kg. of finely crushed seeds were exhaustively extracted with benzene in a large extraction flask and on removal of the solvent by distillation 118 g. of an oil of the consistency of honey were obtained. It was obtained as a transparent light brown liquid on purification by Fuller's earth and animal charcoal.

Examination of the Oil.—It is a semi-drying oil, free from nitrogen or sulphur and optically inactive. It burns with a partially smoky and non-sooty flame. It has specific gravity 0·9229 at 22°; refractive index, 1·3795 at 30°; solidifying point, −11°; acid value, 11·2; saponification value, 193·1 ; acetyl value, 14·8 ; iodine value 95·6 ; Hehner's value, 93·9 and unsaponifiable matter, 1·7%.

75 G. of the oil were saponified with alcoholic alkali and the soap extracted with ether to remove the unsaponifiable matter. The fatty acids were extracted with petroleum ether after acidifying the soap solution with dilute sulphuric acid. These were semi-solid and had liquifying point 35-38°.; specific gravity, 0·8931 at 40°; neutralisation value, 192·5; mean molecular weight, 291·4 and iodine value, 104·8. 40 G. of these fatty acids were subjected to Twitchell's lead salt-alcohol method and separated into saturated and unsaturated portions (Twitchell, *Ind. Eng. Chem.*, 1921, **13**, 806). Table I gives the percentages.

TABLE I.

Acids.	In mixed acids.	In oil.	Iodine value.	Mean M. W.
Saturated .	21·7%	20·01%	1·6	260·8
Unsaturated	78·3	72·19	141·6	280·5

Examination of Unsaturated Acids.—The methods of estimation according to Eibner and Muggenthalor (Lewkowitch, "Chemical Technology of Oils etc.", 5th Ed., Vol. I, p. 573), and Jamiesson and Boughman (*J. Amer. Chem. Soc.*, 1920, **42**, 1197) failed as no crystalline bromo derivatives were formed. By oxidation with alkaline potassium permanganate (Leukowitch, *ibid.*, 1904, Vol. I, p. 360) the presence of oleic and linolic acids alone was proved and these, therefore, may be presumed to constitute the unsaturated portion of the fatty acids for all practical purposes. From the iodine value the percentages of these acids have been calculated and are given in Table II.

TABLE II.

Acids	In unsaturated acids.	In mixed acids	In oil.
Oleic ..	42·8%	33·5%	30·9%
Linolic .	57·2	44·8	41·3

Examination of Saturated Acids.—The mixed saturated acids were esterified and the methyl esters fractionally distilled under reduced pressure, the pressure and temperatures being recorded. The weights of the various fractions and their iodine and neutralisation values gave the percentages of stearic and palmitic acids in the mixture. The mean molecular weights of the first and the last fractions were found to lie between 270·3 and 298·4, the mean molecular weights of methyl palmitate and stearate respectively. Table III gives the results of distillation and Table IV those of analysis.

TABLE III.

Fraction.	Temperature.	Pressure.	Weight.
I	167-170°	5 mm.	2·58 g.
II	170-172° rose quickly to 183°	,,	3.20
III	183-186° rose to 190-200°	,,	0·72
Residue	Above 200°.	,,	1·42

TABLE IV.

Fraction.	Iodine value.	Sapon. value.	Mean M. W.	Acids					
				Palmitic.		Stearic		Unsaturated.	
I	1·3	204·6	274·3	2·00 g.	77·52%	0·40 g.	15·51%	0·043 g	1·66%
II	1·8	199·3	281·5	1·74	54·56	1·22	38·42	0·074	2·30
III	3·5	192·1	291·8	0·17	24·63	0·48	69·56	0·032	4·48
Residue	13·2	189·7	295·4	0·082	7·08	1·03	88·20	0·240	16·9

Examination of the Unsaponifiable Matter.—This was extracted by ether after saponification of the oil with alcoholic caustic potash. On purification by repeated crystallisation from alcohol it was identified as a phytosterol, m.p. 131-33°.

One of the authors (R. N. M.) is highly indebted to the 'Kanta Prasad Trust' of the Allahabad University for grant of a scholarship which enabled him to undertake the present investigation.

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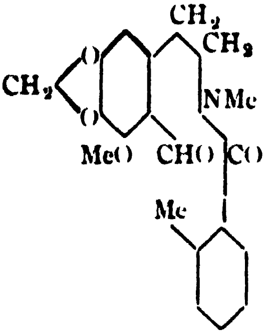
STUDIES IN THE COTARNINE SERIES. PART IX. ATTEMPTS TO SYNTHESISE ALKALOIDS OF THE CRYPTOPINE TYPES.

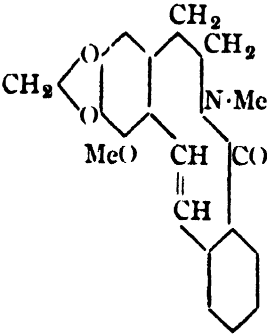
By B. B. Dey and (Miss) P. Lakshmi Kantam.

The aim of the large variety of experiments which were undertaken under this caption was to effect the closure of a second *iso*quinoline ring on to that of cotarnine thus producing the skeleton of the structure of the molecules of the protopine and berberine alkaloids. Some of the results are now recorded. It would be seen that although, as a rule, the reactions proceeded smoothly in the beginning, attempts at ring-closure at the final stage have hitherto been unsuccessful.

Cotartine was condensed with *o*-toluoyl chloride (b.p. 213°/760 mm.) to *o*-toluoylcotarnine, m p. 99-100° (I) which was obtained in excellent yield and which showed the presence of a free and reactive aldehyde group by the formation of a crystalline oxime (m.p. 170°), semicarbazone (m.p. 200°) and hydrazone (m. p. 211°).



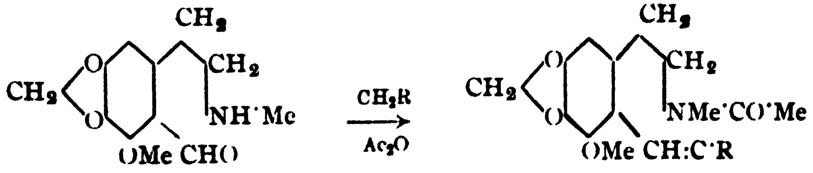
(I)



(II)

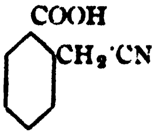
Although, assuming structure (I) to be correct, the relative orientation of the methyl and the aldehyde groups would make the prospect of interaction between them seem reasonably certain, our expectations were not realised and all attempts in the direction of closing the ring (II) ended in failures. Different condensing agents, *e.g.*, dilute alkalis, sodium ethoxide, HCl gas, phosphorus pentachloride, phosphorus oxychloride, etc., were tried but they led in almost all cases to the recovery of unchanged materials at the end. Proceeding next with the assumption that the methyl hydrogen atoms required to be activated, *e.g.*, by the introduction of a halogen atom or a CN-group or a nitro-group, bromotoluoyl bromide, ω-cyano-*o*-toluoyl chloride and *p*-nitro-*o*-toluoyl chloride (3-nitro-6-methylbenzoyl chloride) were prepared, the first by the bromination of *o*-toluoyl chloride according to the process described by Davis and Perkin (*J. Chem. Soc.*, 1922, **121**, 2202), the second from phthalide and potassium cyanide, and the third from *p*-nitro-*o*-toluidine through the nitrile and the acid. The interaction of cotarnine with these compounds was tried under different conditions. The first two gave unstable oily products which were readily decomposed into cotarnine on attempting to condense them in the presence of alkalis or dehydrating agents. *p*-Nitro-*o*-toluoyl cotarnine was, however, obtained easily as crystals (m.p. 125°), which formed a crystalline oxime and semicarbazone indicating the presence of a free aldehyde group, but all efforts to condense it to the desired ring structure proved fruitless.

In further continuation of this work, it seemed desirable to investigate the possibility of closing a second *iso*quinoline ring on to that of cotarnine by condensing the latter base with compounds containing a reactive methylene group, in the presence of acetic anhydride. Some of the experiments carried out with this end in view are described briefly in this paper, attempts being made to condense cotarnine with homo-phthalonitrile, phthalide, nitrophthalide, meconine and nitromeconine. Dutt and Seshacharyulu (*Proc. U. P. Acad. Sci.*, 1934, **4**, 159) have studied the condensation of cotarnine with several compounds containing a reactive methylene group such as hippuric acid, benzyl cyanide, phthalide, etc., under similar conditions. On the assumption that in the presence of acetic anhydride, the secondary base gets instantly acetylated, thus preventing the imino-group from taking part in the condensation and leaving the aldehyde group alone free to react, as in a Claisen's or a Knoevanegal's reaction, the following constitution has been assigned to the condensation products :—

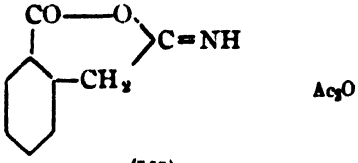


(III) (IV)

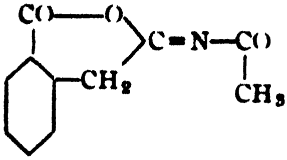
The condensation of cotarnine with homo-phthalonitrile (V) in the presence of acetic anhydride gave a compound, m.p. 245°, insoluble in dilute acids and slowly dissolving in dilute sodium hydroxide. The results of analysis of this compound were found to be in agreement with those required for the acetyl derivative of homo-phtholonitrile (VII) and not the expected "anhydroacetylcotarnino-homo-phthalonitrile" (VIII).



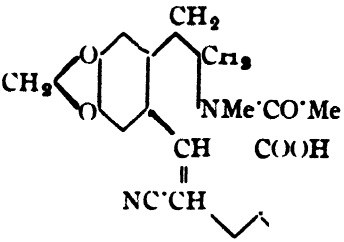
(V)



(VI)



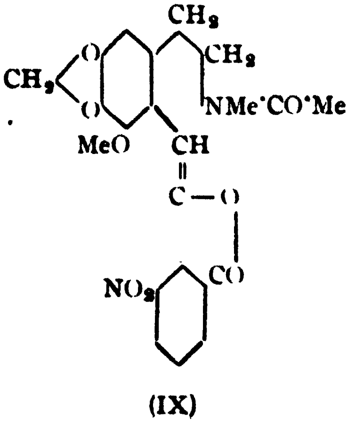
(VII)



(VIII)

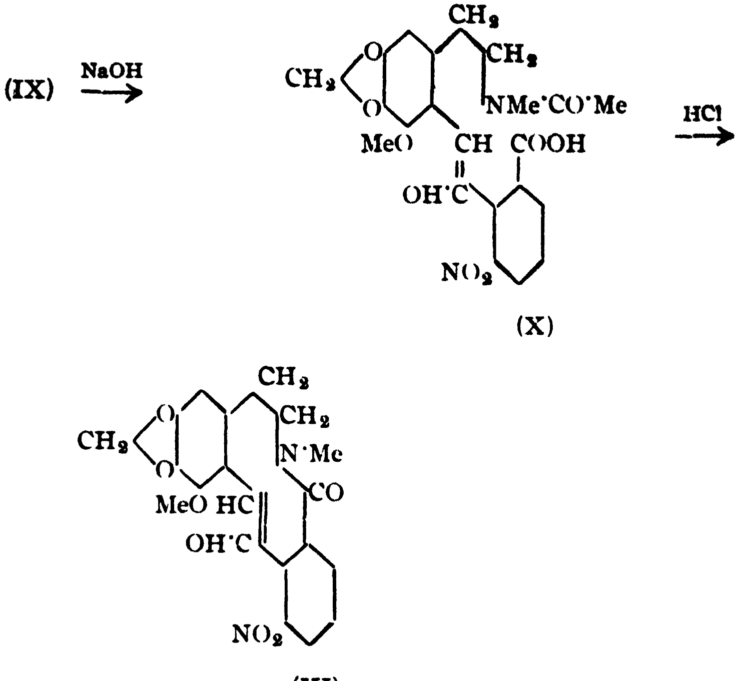
The identity of the compound formed in this reaction with (VII) was also proved by (*i*) hydrolysing it with dilute hydrochloric acid when homophthalic acid (m.p. 180°) was obtained, and (*ii*) by synthesis from homophthalonitrile by the action of acetic anhydride (*vide supra*).

5-Nitrophthalide, on the other hand, was found to condense with cotarnine in the presence of acetic anhydride yielding the expected 'anhydroacetylcotarnino-5-nitrophthalide' (IX) melting at 165°, insoluble in dilute acids and slowly dissolving in sodium hydroxide.



(IX)

It was expected that the acid (X), obtained from the compound by treatment with hot alkali, should be capable of being deacetylated with dilute acids, thus mäking the closure of a second *iso*quinoline ring possible :



(X)

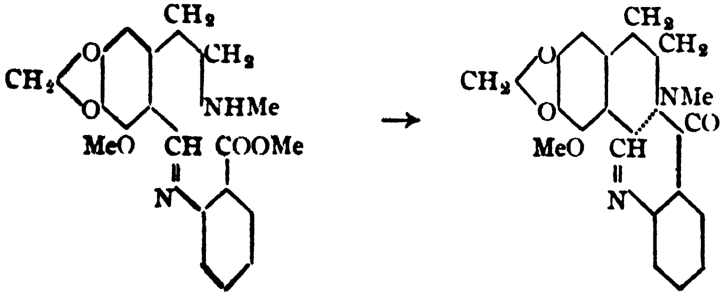
(XI)

Deacetylation with warm dilute hydrochloric acid resulted in a clear solution from which on basification only cotarnine could be recovered.

It has to be recorded here that all attempts to prepare 5-nitro-homophthalonitrile were unsuccessful. The nitrile could be prepared neither by fusing a mixture of 5-nitrophthalide and potassium cyanide as in the preparation of homo-phthalonitrile, nor by refluxing a mixture of 5-nitrophthalide and alcoholic potassium cyanide ; complete decomposition took place in the former case, while in the latter the original product was recovered unchanged.

It was further noted that the expected condensations could not be carried out either with phthalide or meconine by heating with acetic anhydride (Dutt and Seshacharyulu, *loc. cit.*). From phthalide was obained a compound (m. p. 196-98°), slowly dissolving in sodium carbonate, which on recrystallisation from alcohol, melted at 201°, and was identified as anhydroacetylcotarninoacetic acid, m. p. 201°, by a mixed melting point with an authentic specimen of the latter. It is to be observed that in these cases, no condensation took place, acetic anhydride reacting alone with cotarnine and yielding anhydroacetylcotarninoacetic acid. Dutt's conclusion, therefore, that the product with phthalide was anhydroacetylcotarninophthalide could not be confirmed.

Lastly attention was directed to the possibilities of synthesising compounds in which the reactive NH_2-group would replace the methylene radicle, the subsequent reaction between the aldehyde and the amino groups being expected to result in the formation of cyclic structure resembling those of the protopine alkaloids but differing from the latter in having a nitrogen atom in place of methine group. Acetyl anthranilic acid from the oxidation of aceto-*o*-toluidide and its chloride were first employed for this purpose, but the chloride was found to decompose rather rapidly under the conditions necessary for a Schotten-Baumann reaction, and later methyl anthranilate was used instead. The condensation of the latter with cotarnine proceeded smoothly, the product being anhydrocotarnine-methylanthranilate, m. p. 136°, having the following probable stauncture (XII) :



(XII) (XIII)

The proximity of the secondary imino-group and the carbomethoxy group encourages the hope that the removal of a molecule of methyl acetate by the action of such dehydrating agents as acetic anhydride, etc., would not present insuperable difficulties. Experiments which are being conducted in this field have not concluded yet.

Experimental.

o-Toluoylcotarnine (I).—Cotarnine was suspended in 2*N*-sodium hydroxide, the required amount of freshly prepared *o*-toluoyl chloride was added and vigorously shaken when a thick oil resulted. The oil was washed well with water containing a little hydrochloric acid and then rubbed with ligroin, when the unreacted toluoyl chloride was removed and the oil gradually solidified. Crystallisation from dilute alcohol (1 : 1) furnished a colourless solid, m.p. 99-100°, yield quantitative. (Found : N, 3·7. $C_{20}H_{21}O_5N$ requires N, 3·94 per cent).

The *Oxime*, prepared in the usual way, crystallised in bunches of flat needles, m.p. 170°. It is readily soluble in dilute sodium hydroxide and is reprecipitated unchanged on acidification (Found : N, 7·41. $C_{20}H_{22}O_5N_2$ requires N, 7·56 per cent).

The *Semicarbazone* crystallised in needles, m.p. 200°, and the *hydrazone*, in soft needles, m.p. 211°.

p-*Nitro*-o-*toluoylcotarnine*.—*p*-Nitro-*o*-tolunitrile (*Ber.*, 1898, **31**, 2880) was obtained in long yellow felted needles, m.p. 105°, by diazotising a suspension of finely divided *p*-nitro-*o*-toluidine hydrochloride, decomposing with potassium cuprocyanide at 70° in the usual way and purifying the product by a process of slow sublimation, yield 3·5 g. of the pure crystals from 10 g. of the toluidine. *p-Nitro-o-toluic acid* (colourless crystals, m.p. 179°) was obtained in quantitative yield by the hydrolysis of the nitrile with 50% sulphuric acid, and the chloride (colourless crystals, m.p. 59°) was paepared in the usual way by heating with thionyl chloride.

Cotarnine (2 g.) was suspended in 2*N*-sodium hydroxide, the required amount of *p*-nitro-*o*-toluoyl chloride dissolved in toluene was added and shaken well. After leaving for 30 minutes, the upper toluene layer was separated, washed once with water and allowed to evaporate spontaneously. The resulting oil was washed with dilute hydrochloric acid in order to remove any of the unreacted cotarnine and rubbed with rectified spirit, when it changed rapidly into a gritty solid. Crystallisation from dilute methyl alcohol gave beady crystals, m.p. 124-25°. The compound is insoluble in dilute acids and alkali. (Found : C, 60·5 ; H, 5·2 ; N, 7·15. $C_{20}H_{20}O_7N_2$ requires C, 60·0 ; H, 5·0 ; N, 7·0 per cent).

The *Semicarbazone*, prepared by the usual method, crystallised in short yellow square plates, m.p. 219-20°. (Found : N, 15·21. $C_{21}H_{23}O_7N_5$ requires N, 15·31 per cent).

The *Oxime* crystallised in beady crystals, m.p. 175° and the *hydrazone* formed thin square plates, m.p. 255°.

The following attempts were made for ring-closure : (*a*) *Sodium ethoxide* : The compound was dissolved in warm absolute alcohol, a few c.c. of sodium ethoxide added and left overnight. (*b*) *Piperidine* : A few drops of piperidine were added to an alcoholic solution of the substance and kept for 24 hours at 40°-50°. (*c*) *Dry* HCl *gas* : The alcoholic solution was saturated with the gas and left for 2 days. (*d*) *Concentrated sulphuric acid* : The substance was dissolved in ice-cold concentrated sulphuric acid, the solution left in the ice chamber for 12 hours and then poured into water. (*e*) *Sodium hydroxide* : 1 c.c. of dilute caustic soda was added to an alcoholic solution of the substance and left for 2 days. In all cases the original compounds were recovered unchanged.

Action of Acetic Anhydride on Homo-phthalonitrile (VII).—Homophthalonitrile (1 g.) was heated under reflux with acetic anhydride (10 c.c.) for 1 hour. On cooling, crystalline solid separated, which was filtered, washed well with water and crystallised from dilute alcohol as a crystalline solid, m.p. 245°. It is insoluble in dilute acids and slowly dissolves in alkali and can not be reprecipitated from the alkaline solution. (Found : N, 6·7. $C_{11}H_9O_3N$ requires N, 6·9 per cent).

Anhydroacetylcotarnino-5-nitrophthalide (IX).—Cotarnine (1 g.), acetic anhydride (10 c.c.) and 5-nitrophthalide (0·89 g.) were refluxed for 1 hour and poured into water when a thick oil was obtained. It was washed well with water and crystallised from dilute alcohol in orange coloured needles, m.p. 165°. It is insoluble in dilute acids. (Found : N, 6·36. $C_{22}H_{20}O_8N_2$ requires N, 6·36 per cent).

Anhydrocotarnino-methyl anthraniiate (XII).—Cotarnine (1 g.) was rubbed with methyl anthranilate (0·64 g.) and left overnight. The hard, light yellow crystalline solid was washed and crystallised from boiling alcohol as colourless crystals, m.p. 136°. It dissolves in cold dilute acids and is reprecipitated on basification. On treatment with acetic anhydride, it decomposes into cotarnine and the acetyl derivative of methyl anthranilate. (Found : N, 7·3. $C_{20}H_{22}O_5N_2$ requires N, 7·56 per cent).

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PHOTOPOLYMERISATION OF FORMALDEHYDE TO REDUCING SUGARS IN VITRO.

By Atma Ram and N. R. Dhar.

In publication from the laboratories, Dhar and collaborators (Dhar and Sanyal, *J. Phys. Chem.*, 1925, **29**, 926; Gopala Rao and Dhar, *ibid.*, 1931, **35**, 1418; Atma Ram and Dhar, *ibid.*, 1932, **36**, 575) have reported the polymerisation of formaldehyde to reducing sugars, when 2 % solutions of formaldehyde to sunlight in sealed glass bulbs for periods varying from 60 to 120 hours in presence of photocatalysts like ferric chloride, chlorophyll, methyl orange, nickel carbonate, zinc oxide, etc. The best results obtained so far are those with ferric chloride. It is interesting to note, however, that formaldehyde solutions when mixed with fluorescent substances like safranin, cartharamin, rhodamin etc., are exposed to sunlight, do not form reducing sugars. Hence most of the experiments described here have been carried on with ferric chloride as a photocatalyst. In the present paper, a brief account of the results obtained is recorded.

EXPERIMENTAL.

Merck's formaldehyde after distillation was used in these experiments, since on keeping for a long time it passes into paraformaldehyde. Dilute solutions of formaldehyde with the requisite amount of ferric chloride were exposed to sunlight in thin layers in petri dishes covered with quartz covers for periods varying from 6 to 8 hours.

When a mixture of formaldehyde and ferric chloride is exposed to light, they react with the result that ferric chloride is reduced to ferrous chloride. The presence of reducing sugars photosynthesised from formaldehyde was tested by Benedict's solution, because Fehling's solution is reduced by formaldehyde also. Since ferrous chloride reduces Benedict's solution, it is necessary to remove ferrous chloride before testing the exposed solutions for reducing sugars.

To the solution after exposure, an excess of ammonia was added to remove the ferrous and ferric salts as hydroxides. The filtrate which contains ammonium salts, urotropine and the synthesised sugars, if any, was concentrated on a water-bath and evaporated to dryness. It was then extracted with methyl alcohol and the solution tested with Benedict's solution. If a reduction was observed, the presence of reducing sugars was confirmed by Molisch's test. The amount of sugars, if sufficient, was estimated by weighing the amount of copper oxide obtained after reduction. The extracted solution was also tested for disaccharides by first hydrolysing with hydrochloric acid and then applying Benedict's test. The solution of ferric chloride should be prepared fresh and should not be acidic, but neutral as far as possible, since the presence of acids is detrimental to the polymerisation of formaldehyde to reducing sugars.

From the researches of Dhar and Palit (*J. Phys. Chem.*, 1925, **29**, 925 ; 1928, **32**, 1262 ; 1930, **34**, 993) it is known that sugars are oxidised when their solutions are exposed to light and that ferric chloride acts as a good catalyst in these oxidation reactions. The photo-conversion of formaldehyde into reducing sugars is a slow process and it is likely that on prolonged exposure in presence of ferric chloride, the sugars synthesised may be partially photo-oxidised. In the following table some of these results are summarised.

TABLE I.

15 C.c. of 4% solution of formaldehyde exposed. Container—Petri dishes covered with quartz covers.

	System exposed.	Amount of sugar as glucose in 100 c.c.		
		7 hr.	10 hr.	15 hr.
1	Formaldehyde with 2 c.c. of N/5-$FeCl_3$	0·0007	0·001	0·0012
2.	,, ,, 3 c.c. ,,	0·001	0·0012	0·0011
3.	,, ,, 0·5 g of pure kieselguhr	Nil	Nil	Nil
4.	Exp. No 3 with both kieselguhr and ferric chloride	0·0013	0·0017	0·002

These results corroborate the previous claim established by us that formaldehyde can be readily converted into reducing sugars in presence of ferric chloride when exposed to light. Kieselguhr in presence of ferric chloride, when exposed to light, appears to be a good surface catalyst and photo-sensitiser for this reaction. It will be interesting to note here that Baly (Faraday Soc. Diccussion on Photo processes, 1931, pp. 545) has prepared efficient photo-catalytic surfaces by depositing aluminium and ferric hydroxide on kieselguhr and obtained good yields of organic matter from carbon dioxide.

Temperature Coefficient of the Photo-formation of Sugars from Formaldehyde in vitro.

In a previous communication (Atma Ram and Dhar, *J. Phys. Chem.*, 1932, **36**, 575) we have reported the temperature coefficient of the polymerisation of formaldehyde into sugars in the presence of ferric chloride. Since a study of temperature coefficient of this reaction has an important bearing on all findings with regard to the mechanism of photosynthesis, these experiments have been extended. In actual practice, the same procedure as described before was resorted to and the solutions were exposed in petri dishes kept at different temperatures. In order that a sufficient amount of sugars may be synthesised and estimations be correct, the solutions were exposed in several petri dishes.

TABLE II.

System exposed—15 c.c. of 4% formaldehyde and 2 c.c. of $N/5$-$FeCl_3$.
Container—Petri dishes covered with the quartz covers.
Exp. No. 5—Blank (15 c.c. of formaldehyde with no ferric chloride).

	Wt. of sugar photosynthesised in g./100 c.c. calc. as glucose.				Temperature coefficients.		
	20°	30°	40°	50°	20-30°	30-40°	40-50°
1.	0·0006	0·001	0·001	0·0008	1·7	1·0	0·8
2.	0·0007	0·0011	0·001	0·00085	1·6	0·9	0·85
3.	0·00075	0·0012	0·00104	0·0009	1·6	0·9	0·86
4.	0·0006	0·0009	0·0009	0·0008	1·5	1·0	0·9
5.	Nil	Nil	Nil	Nil	..	...	...

An examination of these results shows that the yield of sugars formed from formaldehyde begins to decrease or at least does not increase above 30°. It will be interesting to note here that the yield of formaldehyde obtained from the photochemical reduction of carbonic acid *in vitro* also begins to decrease beyond 30°.

DISCUSSION.

From an account of the results given in the preceding pages it will be seen that a solution of formaldehyde is not easily polymerised to sugars in the absence of photocatalysts in sunlight, but in the presence of ferric chloride, reducing sugars are obtained even after an exposure of 6 hours. The yield of formaldehyde photosynthesised from carbon dioxide and water is not as high as that of polymerised sugars from the former in presence of ferric chloride. It appears that the first stage in photosynthesis is more difficult to be accomplished than the second one.

It seems that surfaces facilitate this photo-conversion of formaldehyde into reducing sugars, since in the presence of kieselguhr and ferric chloride, the yield of photosynthesised sugars is more than in the presence of ferric chloride alone. Recently Baly and collaborators (*Proc. Roy. Soc.*, 1935, **B117**, 218) have succeeded in preparing photocatalytic surfaces, which have a marked photosynthetic activity by depositing freshly precipitated aluminium hydroxide, ferric and chromic hydroxides with small amounts of thorium hydroxide on finely powdered kieselguhr. That photosynthesis is essentially a heterogeneous photocatalytic reaction, appears to be supported by our experiments.

The effect of temperature on the photopolymerisation of formaldehyde into reducing sugars is in accordance with its effect upon the photochemical reduction of carbon dioxide to formaldehyde and photosynthesis *in vitro*. The yield of reducing sugars is more at 30° than at 20°, whilst at 40°, the amount of sugars photosynthesised begins to show a tendency to decrease with the result that at 50 , the temperature coefficient becomes less than unity. The explanation of this observation appears to be the same as advanced by us in the case of photosynthesis of formaldehyde from carbon dioxide investigated *in vitro*. It is probable that at a higher temperature the actual amount of sugars photosynthesised may be more, but on account of their photo-oxidation, which is proceeding simultaneously, being more pronounced at higher temperatures, the actual yield determined is less; that is why a temperature coefficient less than unity has been observed.

In this connection it will be interesting to note here that Baly has observed a decrease in the yield of organic matter photosynthesised from carbon dioxide beyond 30° *in vitro*; also van Amstel (1916) obtained the value 1·25 for a 10° rise of temperature between 24° and 36·5° in photosynthesis with *Elodeay* and Sir J. C. Bose obtained the value 1·22 for a 10° rise between 20° and 30° in photosynthesis with *Hydrilla*.

The authors are of opinion that a slow speed of the photo-conversion of formaldehyde into reducing sugars investigated *in vitro* may be due to the different nature of formaldehyde produced in the plants from that of the laboratory stuff. In the plants it may be in the activated state and be easily converted into sugars. Even *in vitro* when just formed it is in the active state and a part of it may be polymerised into sugars and another converted into the ordinary inactive variety.

Baly and Barker have differentiated this form of formaldehyde from the ordinary one by assigning to it a different structural formula ($HCOH$). However, recently Baly has assumed the formation of activated formaldehyde as the first product of carbon assimilation *in vitro*. It is difficult to state definitely whether formaldehyde itself polymerises into sugars or requires an extra amount of energy. However, the results recorded here show that ferric salts are efficient photocatalysts in accomplishing the second stage in photosynthesis. This may be one of the functions of iron salts present in the plant.

SUMMARY.

1. Photo-conversion of solutions of formaldehyde (4%) into reducing sugars in the presence of ferric chloride has been observed, when the solutions are exposed to sunlight for about eight hours contained in petri dishes.

2. Finely powdered kieselguhr appears to be a good surface catalyst for this reaction.

3. The amount of reducing sugars photosynthesised is greater at 30° than that at 20°, and at 40°, there does not appear to be any appreciable increase or decrease, whilst at 50 the yield decreases.

4. The results on the temperature coefficient of the photoformation of sugars from formaldehyde *in vitro* appear to show that the effect of temperature on photosynthesis as investigated *in vitro* and *in vivo* is similar.

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HALOGENATION. PART XVII. BROMINATION AND IODINATION OF DIPHENYL.

By Phuldeo Sahay Varma and M. Krishnamurti.

Bromo and iodo derivatives of diphenyl have been obtained indirectly from benzidine and by the use of Ullmann's reaction (*Annalen*, 1904, **332**, 57). Bromo derivatives have been obtained by direct bromination also (Scholl and Neovius, *Ber.*, 1911, **44**, 10). 4:4′-Diiododiphenyl has been obtained by the action of sulphur and iodine in presence of nitric acid (Wilgerodt and Hilgenberg, *Ber.*, 1909, **42**, 3826).

We have studied the action of bromine and iodine on diphenyl in presence of (*a*) fuming nitric acid, (*b*) fuming sulphuric acid or a mixture of both, (*c*) sodium nitrite and fuming sulphuric acid, and (*d*) a mixture of fuming nitric and nitrosulphonic acids. Under these conditions a smaller amount of bromine is required and even iodine acts directly. 4:4′-Dibromo- and 4:4′-diiododiphenyl is obtained in good yield and 2:2′-dibromodiphenyl in small quantities as a bye-product

EXPERIMENTAL.

4:4′-*Dibromodiphenyl.*—A solution of diphenyl (5 g.) in carbon tetrachloride (15 c. c.), bromine (3 c.c.) and sodium nitrite (5 g.) were heated on a water-bath with a reflux condenser and fuming sulphuric acid (15 c c.) was added gradually to the mixture. The contents of the flask were heated for 3 hours and then allowed to stand overnight. The liquid portion was removed from the flask and washed free from acid and carbon tetrachloride distilled off. A residue was obtained (0·3 g.) which was found to be 2:2′-dibromodiphenyl, m.p. 81°.

The solid portion was washed free from acid and unused diphenyl was removed by washing with alcohol. It is crystallised from glacial acetic acid and is found to be 4:4′-dibromodiphenyl (6·2 g.), m.p. 164°.

4:4′-*Diiododiphenyl* was obtained from diphenyl (5 g.) dissolved in acetic acid (15 c.c.), iodine (10 g.) and nitrosulphonic acid (5 c.c.), the last being added from the top of the condenser drop by drop and the whole heated for about 2 hours on a water-bath. After being washed, dried and crystallised from glacial acetic acid it melted at 202°, yield 6·2 g.

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Received September 8, 1936.

HALOGENATION. PART XVIII. HALOGENATION OF ETHYLBENZENE.

By Phuldeo Sahay Varma, Vishwanath Sahay
and B. Ram Subramonium.

The halogenation of ethylbenzene has been studied before and according to the conditions of the experiments which are well known, nuclear or side-chain substitution products are obtained.

We have studied the action of bromine and iodine on ethylbenzene in presence of fuming nitric acid, nitrosulphonic acid or their mixtures and have obtained both nuclear or side-chain derivatives. Ethylbenzene, when chlorinated in presence of iodine, yields 4-chloroethylbenzene in good yield. Using these methods of halogenation, we have obtained the following hitherto unknown halogen derivatives of ethylbenzene : 4-iodo-3-bromoethylbenzene, 4-chloro-3-bromoethylbenzene, and 4-chloro-1′ (?)-bromoethylbenzene.

EXPERIMENTAL.

4-Chloroethylbenzene.—Dry chlorine was passed for 3 hours through ethylbenzene (15 c.c.) in a flask, protected from light either by covering it thickly with soot or with black cloth, in presence of iodine (0·1 g.). The product was washed, dried over calcium chloride, filtered and distilled. A small quantity of unused ethylbenzene distilled over first and then a liquid (11 c.c.) at 180-181°. It gives on oxidation with nitric acid 4-chlorobenzoic acid.

1′-Bromoethylbenzene.—Ethylbenzene (10 c.c.) was taken in a flask which was directly exposed to the sun and then nitrosulphonic acid mixture (about 8 drops) and afterwards bromine (2 c.c.) dissolved in acetic acid (10 c.c.) were added drop by drop and the flask shaken vigorously after each addition. When the whole of the bromine solution was added, the flask was allowed to stand in sunlight for a further period of 1 hour after which it was heated on a water-bath for 1 hour more. The contents were washed with water, dried and distilled. Unused ethylbenzene (3 c.c.) first distilled over and then 4-bromoethylbenzene (a small quantity only) at 188-198°, leaving behind a somewhat viscous liquid which decomposes on further heating. This fraction distills undecomposed at 94-95°/10 mm. It is found to be 1′-bromoethylbenzene, yield 4 g.

4-Bromoethylbenzene and 2 : 4-Dibromoethylbenzene.—The preceding experiment was repeated keeping the flask covered with black cloth instead of being exposed to the sun. The products were separated as described above and distilled at the ordinary pressure when 4-bromoethylbenzene (6 c.c.) distilled over. By brominating ethylbenzene (20 c.c.) with exeess of bromine (12 c.c.), a solid compound (8· 5 g.) was obtained which crystallises from alcohol in needles, m.p. 70-72°. On oxidation this compound gives 2 : 4-dibromobenzoic acid, m.p. 167°. Hence the new compound is 2 : 4-dibromoethylbenzene. (Found : Br, 60·18. $C_8H_8Br_2$ requires Br, 60·58 per cent). It is sparingly soluble in rectified spirit, easily soluble in ether, carbon tetrachloride, benzene and chloroform.

4-Iodoethylbenzene.—Ethylbenzene (10 c.c.), iodine (10 g.) dissolved in acetic acid (20 c.c.) were heated with a reflux condenser on a water-bath and a mixture of fuming nitric and nitrosulphonic acid (6 c.c.) was gradually added. After heating for 4 hours, the reaction product was washed free from acid, dried and distilled at 112-113°/20 mm., yield 10 g.

In this experiment in place of a mixture of fuming nitric and nitrosulphonic acid, fuming nitric acid (3 c.c.) alone, or a mixture of fuming nitric and fuming sulphuric acid (3 c.c. each) or sodium nitrite (10 g.) and fuming sulphuric acid (10 c.c.) can also be employed.

4-Iodo-3-bromoethylbenzene.—4-Iodoethylbenzene (5 c.c.), bromine (3·3 c.c.) and iodine (0·1 g) were heated on a water-bath, when there was a brisk evolution of hydrogen bromide. When the reaction was over after 3 or 4 hours, the contents of the flask were cooled, ·washed with water, sodium carbonate solution and finally again with water, dried and allowed to stand. Needle shaped crystals (3·4 g.) gradually separated out, m.p. 88-89°. It is soluble in alcohol, carbon tetrachloride, ether and chloroform. It gives on oxidation with chromic acid in acetic acid 4-iodo-3-bromobenzoic acid, m.p. 239-40°. Hodgson and Beard (*J. Chem. Soc.*, 1927, 27) gives 242-43° as the melting point of this compound. [Found : Total halogen calc. as Br, 59·1 (by analysis of silver halides) ; Br, 25·9; I, 40·1. C_8H_8BrI requires total halogen, 59·6; Br, 25·7; I, 40·8 per cent].

4-Chloro-3-bromoethylbenzene.—4-Chloroethylbenzene (10 c.c.) was treated with a solution of bromine (4 c.c.) in acetic acid (10 c.c.) in presence of a trace of iodine and heated on a water-bath for 5 hours. The products were then cooled and washed with 1% sodium carbonate, dried and distilled at 143-44°/10 mm. The liquid (5 c.c.), on oxidation with concentrated nitric acid gives 4-chloro-3-bromobenzoic acid, m.p. 213°. Cohen and Raper (*J. Chem. Soc.*, 1904, **85**, 1269) gives 214° as the m.p. of this compound whereas Hodgson and Beard (*loc. cit.*) gives 215-16°. (Found : Total halogen calc. as Cl, 37·0 ; Cl, 16·7 ; Br, 35·1. C_8H_8ClBr requires total halogen calc. as Cl, 37·3; Cl, 16·2 ; Br, 36·4 per cent).

4-Chloro-1'-bromoethylbenzene.—4-Chloroethylbenzene (10 c.c.) was treated with a solution of bromine (5 c c.) in chloroform (5 c.c.) in a silica flask and kept exposed to sunlight when a vigorous reaction set in with a considerable rise in temperature. When the action subsided, the products were washed, dried and distilled at 120-21°/8 mm. The liquid obtained (7 c.c.) gives on oxidation with concentrated nitric acid 4-chlorobenzoic acid, m.p. 243°. It is sparingly soluble in rectified spirit, easily soluble in ether, chloroform and benzene. (Found : Total halogen calc. as Cl, 37·1; Cl, 16·8; Br, 35·2. C_8H_8ClBr requires total halogen calc. as Cl, 37·3; Cl, 16·2; Br, 36·4 per cent).

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INTERPRETATION OF ADHESION TENSION DATA.

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When the surface of a solid is in equilibrium with a liquid—vapour interface making a finite contact angle with the solid surface, the well known Young's equation (*Phil. Trans.*, 1805, **95**, 65) gives the relation.

$$S_{10} - S_{12} = S_{02} \cos \theta_{02} \qquad \ldots \quad (i)$$

*where S = Specific free energy of an interface.
o = Vapour.
1 = Solid.
2 = Organic liquid making an acute contact angle with the solid under investigation.

* The other symbols used in this paper are :—
3 = Water.
4 = Organic liquid having a zero contact angle.
10 = Solid—vapour interface.
12 = Solid—organic liquid interface.
13 = Solid—water interface, etc., etc.
S_{xy} = Specific free energy of xy interface (x or y may be 0, 2, 3 or 4).
θ_{xy} = The angle made by the interface xy with the solid, and measured from the interface towards the solid in the direction xy.

Defining θ_{xy} as above avoids the confusion that arises otherwise (*cf.* Equations connecting A_{12}, A_{13} and θ_{23}, Bartell and Osterhoff, "Colloid Symposium Monograph", 1927, **5**, 113; *J. Phys. Chem.*, 1933, **37**, 548). Moreover it enables one to write down the equations for equilibria at other interfaces merely by symmetry.

Freundlich ("Colloid and Capillary Chemistry", 1926, p. 157) calls $S_{10} - S_{12}$, the adhesion tension A_{12} of the liquid against the solid. Bartell and co-workers (*Ind. Eng. Chem.*, 1927, **19**, 1277; *J. Phys. Chem.*, 1932, **36**, 1178; 1934, **38**, 495; 1935, **39**, 11) have described several methods of determining the adhesion tension of liquids. They have further emphasised on the usefulness of these measurements in the determination of (*a*) the free energy of immersion of a solid in a liquid, (*b*) the adsorption at solid—liquid interfaces, and (*c*) the specific surface of adsorbents. The present paper deals with certain theoretical difficulties that arise in the interpretation of adhesion tension data.

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* The conjugated suffixes 0—4 denote the interface of different phases.

The Adhesion Tension of a Non-spreading liquid, i.e., one which makes a finite Contact angle with the Solid.—Harkins and Dahlstrom (*Ind. Eng. Chem.*, 1930, **22**, 900) makes a careful distinction between what they call, the final free energy of immersion and the total free energy of immersion. The latter quantity is defined as the free energy change that accompanies the immersion of a unit surface of the *dry* solid in the liquid. On the other hand, the final free energy of immersion represents the free energy change brought about by immersing a unit area of *the solid surface in equilibrium with the saturated vapour of the liquid*, into the liquid phase. Harkins has clearly shown that the adhesion tension of a non-spreading liquid is a measure of the *final* free energy of immersion.

The Adhesion Tension of Water against a Solid which is completely wetted by it, i.e., a Solid against which its Contact angle is zero.—For any liquid making a zero angle of contact with a solid, the adhesion tension as calculated from equation (*i*) becomes equal to the surface tension of the liquid; this result is as it ought to be since a solid in equilibrium with the vapour of such a liquid gets a continuous adsorption layer of the fluid; the solid surface thus covered with the adsorbed film behaves like the surface of the liquid for all practical purposes in accordance with Langmuir's principle of independent surface action (*Chem. Rev.*, 1921, **6**, 647). Thus the immersion of such a solid surface into the liquid involves the same free energy change as the immersion of an equivalent liquid surface. Bartell and co-workers have suggested that equation (*i*) should not be used to compute the adhesion tension of a spreading liquid. They are of the opinion that the adhesion tension of water against a solid (with which it makes a zero angle of contact) is obtained by measuring θ_{23}, the angle of contact made by the water—non-spreading organic liquid interface with the solid and calculating by means of the equation

$$A_{13} \text{ (of Bartell)} = A_{12} + S_{23} \cos \theta_{23} \qquad \ldots \qquad (ii)$$

The exact interpretation of A_{13} of Bartell could be had thus : by the application of Yonng's relation to the solid—organic liquid—water system we get

$$S'_{12} - S'_{13} = S_{23} \cos \theta_{23} \qquad \ldots \qquad \ldots \qquad (iii)$$

S'_{12} is the interfacial tension of the interface between the solid and and the organic liquid, 2, saturated with water and S'_{13} is that of the interface between the solid and the water saturated with the non-spreading organic liquid. Combining equations (*iii*) and (*i*) we get

$$A_{13} \text{ (of Bartell)} = A_{12} + S'_{12} - S'_{13} \qquad \ldots \quad (iv)$$

We could put this equation in the form

$$A_{13} \text{ (of Bartell)} = A_{12} + (S'_{10} - S'_{13}) - (S'_{10} - S'_{12})$$

where S'_{10} is the surface tension of the solid in equilibrium with the vapour of the saturated solution of water in the organic liquid. Thus the A_{13} of Bartell is equal to the final free energy of immersion of the solid in the *anhydrous* non-spreading organic liquid minus the final free energy of immersion of the solid in the nonspreading organic liquid *saturated with water* plus the final free energy of immersion of the solid in water saturated with the organic liquid. Thus the quantity designated by Bartell as the adhesion tension of water is an extremely complicated quantity and does not appear to have the significance attached to it.

The Adhesion Tension of a Spreading Organic Liquid against a Solid; i.e., a Solid against which its Contact angle is zero.—Bartell suggests that A_{14}, the adhesion tension of a spreading organic liquid is to be got by determining the angle of contact made by the water-organic liquid interface with the solid and calculating by means of the equation

$$A_{14} \text{ (of Bartell)} = A_{13} \text{(of Bartell)} - S_{43} \cos \theta_{43} \qquad \ldots \quad (v)$$

Reasoning as before, the A_{14} of Bartell can be shown to be an extremely complicated quantity (since it can be expressed as the algebraic sum of eight free surface energy terms).

The Explanation of the Observation of Bartell that " The order of decrease of the free surface energies when a polar solid is wetted by each of a series of zero Contact angled Liquids is the same as the order of decrease in free surface energies which occurs when water is brought into contact with the same series of liquids" (Bartell and Hershberger, *Ind. Eng. Chem.*, 1930, **22**, 1304; Bartell and Osterhoffs, *J. Phys. Chem.*, 1933, **37**, 548).

Though the A_{14} values of Bartell have a complicated significance as pointed out in the last section, the values for any set of organic liquids exhibit a striking regularity. If one arranges the organic liquids in the order of increasing A_{14} values, the same is found to be true of that of dereasing S_{43} values also. This interesting correlation can be explained thus. It is to be noted that A_{14} values are obtained by means of equation (*v*). Since A_{13} is a constant, the order of increasing A_{14} values is same as the order of decreasing S_{43} cos θ_{43} values. The latter quantity is really the difference of the free energy of immersion of the solid (in equilibrium with water and the organic liquid vapours) against the water layer on the one hand and the organic liquid layer on the other. It is well known that liquids similar to water have small interfacial tensions against water, whereas others have high values. The lower the value of S_{43}, the greater will be the similarity in properties of the water and the organic liquid layer and θ_{43} would approch 90° and cause a decrease of values of cos θ_{43}, since θ_{43} is acute. The order of decrease of values of S_{43} for a series of liquids would thus be more or less the same as that for the values of cos θ_{43}. Hence the values of S_{43} cos θ_{43} would also be of the same order. Therefore the order of increase of A_{14} values and that of increase of A_{34} (or $S_{30}-S_{43}$) values are one and the same. This is what is implied in the statement of Bartell.

Calculation of Adsorption at Solid-liquid Interfaces from Adhesion tension Data.—In order to calculate adsorption at solid—liquid interfaces Bartell and co-workers (*J. Amer. Chem. Soc.*, 1933, **55**, 466) apply Gibbs equation and derives the relation

$$U=\frac{1}{RT}\,\frac{dA_{14}}{dlnC} \qquad \ldots \qquad \ldots \qquad \ldots \qquad (vi)$$

wher U is the Gibbs' adsorption excess, and C is the concentration of the solute in the organic liquid. In deriving this they assume that $A_{14}=S_{10}-S_{14}$ which is obviously not true as shown in third section of the present paper. Thus the values of U do not represent adsorption at the solid—liquid interfaces. It is however found that the U values thus obtained exhibt an interesting correlation to the adsorption at a water—organic liquid interface; we shall proceed to explain why such a correlation obtains. Combining equations (*v*) and (*vi*) we get

$$U=-\frac{1}{RT}\,\frac{d(S_{43}\cos\theta_{43})}{d\,lnC} \qquad \ldots \qquad (vii)$$

Considerations similar to those discussed in the last section make it evident that the order of decrease of value of U as given by equation (*vii*) (for any series of liquids) ought to be the same as the order of decrease of the values of the expression

$$-\frac{1}{RT}\,\frac{dS_{43}}{dlnC}.$$

The latter expression is a measure of the adsorption at the water—organic liquid interface. This accounts for the observation of Bartell that "The order of maximum adsorption of a given solute from a series of organic liquids was found to be the same whether silica or water was used as the adsorbent."

That adhesion tension data do not give an idea of the adsorption at the solid—liquid interface becomes evident when one considers the adsorption on silica from ethyl carbonate—benzene mixtures. Bartell's data on adhesion tension (Bartell and Fu, *J. Phys. Chem.*, 1929, **33**, 1765) indicate that on silica, ethyl carbonate is selectively adsorbed over the entire range of concentrations. Bartell's own experiments with silica gel (*J. Amer. Chem. Soc.*, 1931, **53**, 2501) give as an S-shaped "apparent adsorption" concentration curve. Apparent adsorption or selectivity, it is to be pointed out, corresponds to the Gibb's adsorption excess (Doss and Rao, *J. Mysore Univ.*, 1935, **8**, 54). Thus there is a disagreement in the adsorption values got from adhesion tension measurements and those got by direct experiments with the silica gel. This difference cannot be attributed to the fact that a plane surface is involved in one case, while capillary action is possible in the other. The effect of proximity of two adsorbing surfaces may now be considered. The closeness as obtained by a capillary of molecular dimensions may mean a greater specificity in adsorption so that in some favourable cases, the finest pores of the adsorbent may be available for only one of the components in the binary mixture. The existence of the finest pores which are accessible to certain substances and not to others may be inferred from Patrick's data on internal gel volumes (Patrick and Opdycke, *J. Phys. Chem.*, 1925, **29**, 601). Silica gel is found to take up more of water than of benzene or carbon tetrachloride. A few of the measurements made by Patrick have been repeated by the present author. A sample of silica gel on being saturated by the dynamic method with each of the following liquids took 0·331 c.c. of water, 0·327 c.c. of ethyl alcohol, 0·306 c.c of benzene, and 0·298 c.c. of carbon tetrachloride per g. of gel. This aspect of the problem has been thoroughly investigated by Rao (*J. Indian Chem. Soc.*, 1935, **12**, 331, 340). Thus a certain amount of space available for water is totally inaccessible for benzene or carbon tetrachloride. Hence, the form of the apparent adsorption-concentration curve would depend upon the nature of the adsorbent. The gel used by Bartell (prepared from nickel silicate) which may be expected to have a large proportion of the wider capillaries showed a lesser capacity for selection (*i.e.*, gave S-shaped curves), whereas the gel used by Jones and Outridge (*J. Chem. Soc.*, 1930, 1574) and B.S. Rao. (*J. Phys. Chem.*, 1932, **36**, 616) which had a larger proportion of finer capillaries showed a greater tendency for selective adsorption. Thus one would expect a plane surface of any solid to exert less selective action than a porous adsorbent. So, the disagreement between the adsorption values obtained from adhesion tension data and those by direct measurement with silica gel could be explained if the membrane used in the displacement pressure method consisted of finer pores. But as the radius of the pore in the membrane used by Bartell was of the order of 10^{-4} cm. one would expect a similar tendency for selective adsorption. Therefore, the discrepancy is probably not due to capillary action.

In this connection Bartell and Fu (*loc. cit.*) said "It should be remarked however that this is not a conclusive proof of the inapplicablity of the Gibbs' theorem as related to the solid—liquid iterface. It is well known that if a substance raises the surface tension of a solvent, the increase is usually very small. If a similar action appears at a solid—liquid interface, the effect of the component with lower adhesion tension may be small when compared with that of one having a higher adhesion tension. The method available at present for the measurement of adhesion tension may not be sufficiently accurate to detect the small increase of adhesion tension due to the addition of a second component (but this is not believed to be the case)". Bartell and Fu treat this anomaly by, what they call a "thermodynamically identical process". It is evident that their procedure is not identical with that of Gibbs' since the conclusions in such a case would have been identical. Thus, their treatment is not rigorous.

There are two other factors to be taken into account while calculating the adsorption from concentrated solutions by making use of Gibbs' equaation. First, the concentrations are not identical with activities at higher concentrations. Secondly, Bartell's relation between Gibbs' adsorption excess and the actual concentration of the adsorbed component in the surface layer involves the assumption that the Gibbs' dividing surface lies at the physical interface. But the simple Gibbs' equation gives the $\Gamma_2^{(1)}$ of Guggenheim and Adam (*Proc. Roy. Soc.*, 1933, **A 139**, 228) in which case, the above condition is satisfied only in the region of dilute solutions At higher concentrations, the relationship between the Gibbs' adsorption excess and the actual concentration in the adsorption layer is not given by the formulation of Bartell.

Calculation of the Specific Surface of Adsorbents.—Bartell and Bartell (*J. Amer. Chem. Soc.*, 1934, **56**, 2205) have suggested a method of calculating the specific surface of porous adsorbents from data on adhesion tension and the heat of wetting. In the calculations they assume that the adhesion tension is a measure of the total free energy of immersion.

But this is not true as shown in the first three sections of the present paper. Moreover, the experimental results of Bartell and Almy (*J. Phys. Chem.*, 1932, **36**, 985) show that the absolute values of heat of wetting calculated from adhesion tension data may differ from the actual values by over twenty per cent. Thus the method of calculating the specific surface does not appear to be quite sound.

Value of Adhesion Tension data.—Whereas the correlation of fundamental quantities such as adsorption and total free energy of immersion to adhesion tension data is beset with theoretical difficulties, the extensive work of Bartell seems to be of great value in getting at qualitative or semi-quantitative ideas regarding wetting phenomena. Bartell and Bartell's later paper (*loc. cit.*) shows several new interesting relations between the experimentally determined quantities, the explanation of which may throw further light on the subject.

SUMMARY.

It is shown that adhesion tension data of spreading liquids cannot give any definite information regarding (*a*) the total free energy of immersion of a solid in a liquid (*b*) adsorption at solid—liquid interface and cannot be used to calculate the specific surface of adsorbents.

In conclusion, the author wishes to thank Professor B. Sanjiva Rao for helpful criticisms.

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STUDIES IN THE COAGULATION OF COLLOIDS. PART XVII. THE ANOMALOUS COAGULATIVE POWER OF AQUEOUS MERCURY CHLORIDE

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The present problem arose out of certain unexpected results to be published shortly, on changes of viscosity and transparency observed in a number of colloids in the presence of some *non-electrolytes*. A consideration of its remarkably low electrolytic conductivity, both in the fused (Biltz, *Z. Physik*, 1926, **36**, 36) and the dissolved state (Carnegie and Burt, *Chem. News*, 1897, **76**, 174; Biltz, *Z. physikal. Chem.*, 1902, **40**, 199) and its Raman effect (Krishnamurti, *Indian J. Phys.*, 1930, **5**, 651) and other properties make one regard mercury chloride as almost a non-electrolyte, behaving principally *covalently*. Its familiar use as an analytical reagent, as also its rôle in not a few inorganic reactions, however, suggests that the other and the opposite electrovalent aspect of its behaviour might not be negligible. It was considered to be of some interest, therefore, to investigate if an examination of its coagulative power would throw some light on the above question. While a definitive decision does not seem permissible at the present stage, the results obtained supply information in a hitherto unexplored line and the complexity of the rôle of mercury chloride has been brought out; the latter was noticed in earlier work on the anomalous changes of the viscosity and transparency in colloids in its presence (Joshi and Kulkarni, *J. Indian Chem Soc.*, 1936, **13**, 439; Joshi and Menon, *ibid.*, 1937, **14**, 103).

EXPERIMENTAL.

The coagulative powers have been examined in the case of eleven colloids in respect of mercury chloride, barium chloride and aluminium chloride. Most of the sols were prepared and their colloid contents determined as described in an earlier paper (Joshi and Jagannath Rao, *J. Indian Chem. Soc.*, 1936, **13**, 217). The gold sol was prepared by adding 10 c.c. of 0·38% of gold chloride solution to 200 c.c. of redistilled water in a Jena flask and made alkaline with 10 c.c. of 0·2 *N*-K_2CO_3. The solution was next heated and when it came to boiling, 5 to 6 c.c. of 0·3% formalin were added drop by drop with continuous stirring. A clear transparent red sol was obtained: this was not dialysed (*vide infra*). A similar method was used to prepare colloidal silver starting with silver nitrate ($N/200$), ammonia and formaldehyde. Fixed volumes (5 c.c.) of the colloid and each of the differently concentrated coagulator solutions were mixed. The reciprocal of C, the coagulator concentration expressed as millimols per litre required just to cause incipient flocculation, denotes the coagulator power. It is known that this quantity depends upon the manner of addition, stirring, etc., the temperature, concentration of the colloid and, therefore, it lacks an absolute value. For purposes of a comparative survey under a given set of conditions and using a fixed procedure, the coagulative powers, thus determined, were found to be sufficiently accurate and reproducible. These results for C, the precipitating concentration and C. P., the coagulative power are shown in Table I.

TABLE I

Sol.	KCl		$BaCl_2$		$HgCl_2$		$AlCl_3$	
	C.	C.P.	C	C.P.	C.	C.P.	C.	C.P.
MnO_2	14·7	67·9	0·2470	4042	0·4296	2328	0·8170	1224·0
As_2S_3	56·3	17·8	0·6400	1563	0 2484	4026	0·08525	1730·0
Fe_2O_3	12·3	81·7	0·7690	1300	0 3141	3184	0·1149	8706·0
Au (un-dialysed)	16·8	59·5	0·2080	4800	0·4014	2492	—	—
Sb_2S_3	39·2	25·5	0·3720	2689	0·2970	3367	0·2333	4286·0
V_2O_5	20·4	49·1	0·2710	3687	0·3956	2528	0·0924	10820·0
Ag (un-dialysed)	8·8	113·7	0·1780	5615	0·1561	6409		
CuS	23·2	43·1	0·7390	1353	0·5347	1870	0·3796	2634
Cu-ferrocyanide	11·1	90·4	0·2520	3968	0·5907	1692	0·1021	9790
Prussian blue	125	7·98	3 48	287	5·051	198	0 5129	1950
CdS	46·6 .	215	0.4450	2247	0·2692	3715	0·07635	

C = precipitating concentration in m. moles ; C. P· = coagulative power.

DISCUSSION.

It is seen from the foregoing results that, as is to be anticipated from general experience (and but partially indicated by the so-called Wetham's law for the relation between C.P., the coagulative power and the valency of the significant ion), there is on the whole a very rapid increase in C.P. according to the series, KCl $<$ $BaCl_2$ $<$ $AlCl_3$. The coagulative power C.P. for mercury chloride is seen to be almost as high as the bivalent barium ion and in not a few cases, distinctly greater. The present stage of development of the theory of the mechanism of the coagulative action does not allow of even a semiquantitative specification of C.P. in terms of known and simpler factors. The well known Hardy-Schulze rule merely gives that the relative precipitating power of an ion increases with (*a*) valency and its (*b*) preferential adsorption. The last quantity is almost entirely a specific property of a given colloid towards an added material. This is well illustrated by the wide variation in C.P. of any one of the four coagulants in respect of the colloids examined. Since neutralisation of the micellar charge represents not only the end but substantially the mechanism of coagulation, and since the colloids now studied were all negatively charged, the kation is the chief coagulant. In this connection it might be recorded that as indicated by the absence of change of viscosity and turbidity, positive ferric oxide sols failed to show any coagulation with aqueous $HgCl_2$ even at high concentrations. The additional determinants of the C. P., besides (*a*) and (*b*) mentioned above are : (*c*) the number of ions per unit volume. This is indicated by the corresponding electrical conductivity, which depends upon the degree of ionisation, ionic charge and the corresponding mobility (reduced viscosity of the medium would appear to favour coagulation usually, though not invariably, *cf.* Joshi and Iyengar, *J. Indian Chem. Soc.*, 1934, **11**, 570) ; (*d*) the state of the micellar, ionic and molecular surface hydration ; (*e*) reduction of the dielectric constant ; (*f*) H-ion concentration of the system ; (*g*) capillary activity, which is a sensible influence only in hydrophyllic colloids ; (*h*) the concentration of the coagulating solution, the colloid strength, its age, temperature, mode of preparation and the mechanical treatment, etc. On general considerations it is seen that (*g*) represents but minor factors, which affect only specially sensitive systems. From data in Table I, the C. P. for $HgCl_2$ appears to be about as high as the bivalent barium and in fact in 6 out of the 11 colloids examined, distinctly greater. This eliminates (*a*) as a principal determinant of the relative C. P. for $HgCl_2$. This also applies to (*h*). For want of relevant data of a detailed character, no deduction can be made in regard to (*e*). Considerable amount of evidence exists however to show that changes in the dielectric constant, whose importance was first brought out by the pioneer work of Kruyt and van Duin (*Koll. Chem. Beih.*, 1914, **5**, 269), especially of Wo. Ostwald (*cf.* Freundlich and Rona, *Biochem. Z.*, 1917, **81**, 87), and in detail by Freundlich ("Colloid and Capillary Chemistry", p. 463), do not possess generality of application (Mukherjee, Chaudhary and Rai Choudhuri, *J. Indian Chem. Soc.*, 1927, **4**, 493 *et seq.* also Joshi and Lal, *ibid.*, 1933, **10**, 247). In regard to (*d*) although mercury salts would appear to be singular in not forming hydrates, data are not available in the literature for inferring the possible effect of this tendency in inducing coagulation. With respect to (*f*) Herstad (*Koll. Chem. Beih.*, 1916, **8**, 399) has observed in a detailed study of the gold sol that the presence of H-ions inhibits appreciably the coagulative action of $HgCl_2$ to an extent dependent on its concentration. It is well known that $HgCl_2$ hydrolyses sensibly in aqueous solutions (Ley, *Z. physikal. Chem.*, 1899, **30**, 226). Herstad (*loc. cit.*) ascribes the C. P. of $HgCl_2$ chiefly to HgO produced by its hydrolysis. In fact, according to him the alkalinity of the medium is essential for $HgCl_2$ to act as a coagulant. It is interesting to add that during these experiments we found that the gold and silver sols prepared by the well known Zsigmondy method producing a small alkalinity could not be coagulated by $HgCl_2$, *if dialysed*. This result is in accord with the supposition that the OH′ ions which are removed during dialysis are essential for coagulation by $HgCl_2$. We consider, however, that alkalinity as the source of the high C. P. of $HgCl_2$ is not entirely satisfactory explanation of all the facts. For example, our results show that the C.P. of $HgCl_2$ is quite high, higher than $BaCl_2$ in such colloids as As_2S_3, Sb_2S_3, CuS, CdS, which are not alkaline and, if at all, faintly acidic. Another fact which goes counter to the above supposition obtains in the case of colloid MnO_2, which contains traces of KOH produced in its preparation. It is seen that the corresponding C. P. for $HgCl_2$ is distinctly less than $BaCl_2$, the contrary is to be expected if alkalinity produces the high C.P. of $HgCl_2$.

The factor (*b*) is undoubtedly important. Hago Morawitz, (*Koll. Chem. Beih.*, 1910, **1**, 501) noted some parallelism between adsorptions on animal charcoal and colloid gold and that $HgCl_2$ is adsorbed notably heavily by the former. These findings, however suggestive, fail to cover many cases showing that C.P. and ionic adsorbability do not always vary concomitantly (Dhar and Ghosh, *J. Phys. Chem.*, 1926, **30**, 628). In this connection it is interesting to point out that Chakravarty and Dhar (*J. Phys. Chem.*, 1927, **31**, 297) found that adsorption per g. of MnO_2 varied in the order, KCl $>$ $BaCl_2$ $>$ $AlCl_3$, which is just the reverse of the order for C.P. (*compare* Weiser, *J. Phys. Chem.*, 1919, **23**, 208). Work is in progress in these laboratories in order to obtain detailed results for the adsorptions of these coagulants by the above colloids, which will be published shortly.

The above consideration of the various factors for the insufficiency, as a general explanation of the relatively high C.P. of $HgCl_2$, had tacitly assumed that $HgCl_2$ was classifiable with KCl, $BaCl_2$ and $AlCl_3$; this is far from being the case, since it is practically non-ionised. This is illustrated by the following values for the specific conductivity for 0·25*N* solutions of $HgCl_2$, KCl, $BaCl_2$: 0·0001649, 0·030698, 0·024358 mho respectively (as determined by Mr. D. N. Solanki in these laboratories). Luther (*Z. physikal. Chem.*, 1901, **36**, 401) finds the following species in a saturated solution of $HgCl_2$ at 25°, the concentration being expressed in mols per litre : $HgCl_2 = 0{\cdot}26$; $HgCl = 0{\cdot}00015$: $H = 0{\cdot}00033$; $Cl' = 0{\cdot}00048$; $Hg'' = 10^{-8}$; $HgCl''_4 = 5 \times 10^{-6}$. It is evident therefore, that the amounts of the significant ionic and molecular material in the mixture are far too low to be an adequate source for the C.P. of $HgCl_2$, especially when it is noted that the corresponding sulutions of KCl and $BaCl_2$ due to their almost complete dissociation contain the relevant ions in comparatively very large amounts. The C.P. for a tri-or tetravalent kation is likely to be relatively very high, presumably much higher than $AlCl_3$ in the case of the latter. The presence of such ions is rendered likely by the claim of Bourion and Rouyer (*Ann. chim.*, 1928, **10**, 263) that aqueous $HgCl_2$ contains products of the following equilibria :

$$(HgCl_2)_3 \rightleftharpoons 3(HgCl_2) \text{ and } (HgCl_2)_2 \rightleftharpoons 2(HgCl_2).$$

The value of this factor is discounted very appreciably since it is almost certain that the corresponding concentrations of these ionic polymers is extremely small. From a review of these facts taken together it can be concluded that the generality of the relatively high C.P. of $HgCl_2$, brought out by our results, can not be ascribed to one or a simple combination of any of the factors postulated in the current theories of the coagulation phenomena, as discussed above, and be best treated as an open question requiring further examination from an experimental stand-point.

SUMMARY.

1. Results are given for C.P. the relative coagulative powers of KCl, $BaCl_2$, $HgCl_2$ and $AlCl_3$ towards negatively charged colloidal solutions of As_2S_3, Fe_2O_3, Sb_2S_3, V_2O_5, CuS, copper ferrocyanide, Prussian blue, CdS and MnO_2, Au,Ag (the last three being undialysed and containing a small quantity of OH').

2. The C.P. for $HgCl_2$ has been found to be about as high as $BaCl_2$ and in 6 out of 11 cases, greater.

3. Contrary to the conclusions of Herstad, alkalinity is not considered as fundamental to the large value of C.P.

4. The possible influence of the valency, adsorption, H° ions, capillary activity, dielectric constant and especially of the available small kationic concentration are discussed and found to be insufficient for a general theoretical explanation.

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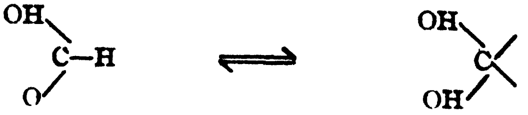
A NOTE ON THE CONSTITUTION OF FORMIC ACID.

BY K. MADHUSUDANAN PANDALAI.

The question of the constitution of formic acid has attracted considerable attention, chiefly because formic acid differs in some of its salient characteristics from the higher homologues in the fatty acid series The highly reducing property of formic acid usually attributed to the presence in it of an aldehyde group is one which stands out prominent in this connection. Ray (*Nature*, 1934, **133**, 646) concludes that the difference between formic acid and its higher homologues is due to the different structure of formic acid in which the hydrogen attached to the carbon is the ionisable atom and not the hydroxyl group as in the case of the higher fatty acids. He shows that the undissociated formic acid and its esters are not reducing agents and attributes the reduction to the formate ions as due to the presence of a "lone pair" of electrons in the carbon atom. Halasyam (*J. Indian Chem. Soc.*, 1935, **12**, 813) quotes other evidence to support this view. This view, however, explains only the strikingly reducing property of the acid leaving unexplained some of the other exceptional properties of the acid, such as its highly acidic character and the absence of a formyl chloride or a formic anhydride

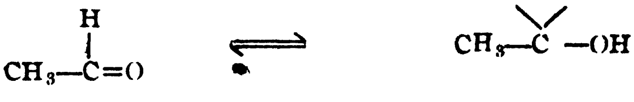
From Raman spectra studies, Venkateswaran (*Proc. Indian Acad. Sci.*, 1935, **2A**, 615) has obtained conclusive evidence for the presence of a "CH" group in the formic acid molecule and of a "CHO" group in the formate ion. This is in agreement with the view put forward by Seshadri (Venkateswaran, *loc. cit.*) that the carboxyl group in the acid is linked to a hydrogen atom (aldehyde group), whereas in the homologues of formic acid the carboxyl is linked to the alkyl groups and that in the course of certain reactions, formic acid is capable of undergoing isomeric change to dihydroxymethylene.

The majority of evidence available from both the physical and chemical properties of the acid tends to confirm the view that there is in formic acid, a "CH" group. This note deals with a very striking piece of evidence in support of this latter view and is based on the well known biological reaction of formic acid studied in detail by Thunberg (*Skand. Arch. Physiol.*, 1920, **40**, 1), and Quastel and Whetham (*Biochem. J.*, 1925, **19**, 520) and Quastel (*ibid.*, 1926, 20, 166). The last named has shown that the activation of formic acid is represented by the simple change,



(I) (II)

in which (I) is the ordinary (or inactive) form of formic acid, while (II) represents the activated form. In view of the presence of two hydroxyl groups in the latter, formic acid should on activation act as a hydrogen donator. Quastel (*et al*) have indeed shown that this is actually the case. Curiously enough formic acid is the most powerful hydrogen donator in the fatty acid series and with the exception of some of the sugars is the most active hydrogen donator yet investigated. It has absolutely no reducing power *in vitro* on methylene blue, even in strongly alkaline solution. Quastel further substantiates the above points by taking substituted formic acid and shows that if for "OH" in (I), a radical acting in the same sense *e. g.*—NH_2 or—CH_3, is substituted, the resulting compounds should also act as hydrogen donators. Thus the activation of acetaldehyde is represented

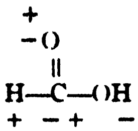


(III) (IV)

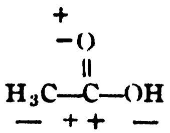
where (IV) should have a powerful attraction for negative electricity. Owing to the non-polar nature of the CH_3-group, there should be an apparent diminution in the reducing power. It has thus been already shown that acetaldehyde is a hydrogen donator under suitable conditions (for example in the presence of *Bacillus coli*). The same is the case with formamide in which the amino group is polar.

Since formic acid has no action *in vitro* on methylene blue, it is clear that as a substrate it is in the inactive state when it does not act as hydrogen donator and the formula (I), must evidently represent the ordinary (or inactive) molecule.

It is known that formic acid is strictly monobasic and it may be asked how the dihydroxymethylene structure, which the substance exhibits on activation (with its two equivalent hydrogen atoms) can satisfy the avowedly monobasic character of the acid. It must, however, be remembered that the carbon of the COOH in formic acid is attached to the hydrogen by one of its negative bonds and to the OH-group by a positive bond, which tends to weaken the whole molecule and incidentally the bond between the hydrogen and oxygen in the OH, thus making possible a greater amount of dissociation, whereas the carbon atom in the higher acid is bound only by positive bonds with consequent greater stability and less dissociation. Thus the structure of formic and acetic acids may be written as follows.



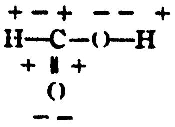
$$\begin{array}{c} + \\ -O \\ \| \\ H-C-OH \\ +\ \ -+\ \ - \end{array}$$



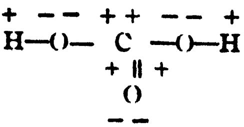
$$\begin{array}{c} + \\ -O \\ \| \\ H_3C-C-OH \\ -\ \ ++\ \ - \end{array}$$

There is, further, absolutely no evidence of the existence of an equilibrium mixture of the type, (I) $\rightleftharpoons$ (II), at any instance comparable to substances which exhibit tautomerism.

It is well known that formic acid cannot lose carbon dioxide, while carbonic acid can. It will be observed in the formula given below that the COOH group in formic acid is negative and in carbonic acid positive.



$$\begin{array}{c} +-+\ --\ + \\ H-C-O-H \\ +\ \|\ + \\ O \\ -\ - \end{array}$$



$$\begin{array}{c} +\ --\ ++\ --\ + \\ H-O-\ C\ -O-H \\ +\ \|\ + \\ O \\ -\ - \end{array}$$

In the former three of the valences of carbon are positive and the fourth negative, while in carbonic acid all four valences are positive. The reducing action of formic acid is thus easily explicable from considerations of its electronic structure.

All these foregoing considerations show that for formic acid to act as a hydrogen donator, it has to get activated or in other words it has to bring about a change in its electronic structure. This occurs when the aldehyde structure of the ordinary acid assumes a dihydroxymethylene structure. Thus the already well known biological property of formic acid, which can be interpreted according to Quastel (*loc. cit.*) as due to a change in the electronic structure of the compound shows that, formic acid has in it a "CH" group when in the normal state changing to a dihydroxymethylene structure on activation. It is thus clear that the ionisable hydrogen is definitely the one attached to the hydroxyl group of formic acid just as in the case of the higher fatty acids and not the one attached to the carbon atom, and the old idea of attributing the exceptional properties of formic acid to the existence in it of an aldehyde group should be retained.

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AN X-RAY INVESTIGATION OF THE CRYSTALS OF DIPHENYLENE DISULPHIDE (THIANTHRENE) AND DIPHENYL DISULPHIDE.

By **Mata Prasad, Jagdish Shanker and B. H. Peermohamed.**

The structure of several crystals of the aromatic compounds containing more than one benzene ring has been recently completely determined and the interatomic distances in many cases are now uniquely known. These substances may broadly be classed into two groups, one in which the rings are fused along a side and the other in which they are either joined end to end or joined through atoms or groups. Of the former the crystal of anthracene (*Indian J. Phys.*, 1930, **4**, 557 ; *Proc. Roy. Soc* , 1933, **A 140**, 79) affords an important example, while the crystals of diphenyl and dibenzyl series (Dhar, *Indian J. Phys.*, 1932, **7**, 43 ; Picket, *Proc. Roy, Soc.*, 1934, **A 142**, 333 ; *Nature*, 1933, **131**, 153 ; Robertson, *Proc. Roy. Soc.*, 1934, **A 146**, 473 ; and Robertson, Prasad and Woodward, *ibid.*, 1935, **A 154**, 187) belong to the latter type.

A study of the crystals of thianthrene and diphenyl disulphide was taken up with a view to find out if any relationship exists between these on the one hand and anthracene, and stilbene and azobenzene, respectively, on the other. In the present investigation only the space groups have been determined by the rotating and oscillating single crystal method using a monochromatic *X*-ray beam ($\lambda = 1{\cdot}54$ Å).

Thianthrene.

Pure thianthrene* was further purified by recrystallisation from carbon disulphide from which well developed crystals were obtained by slow evaporation. When viewed through transmited light, the crystals as well as the solution show a band of beautiful colours indicating their large dispersive power. The melting point of the crystals was found to be 154° and the specific gravity, determined by the flotation method, 1·442. The crystals belong to the monoclinic prismatic class and the a {100}, c{001} and r {101} faces are the predominant ones. The axial ratio determined by crystallographers is

$a : b : c : : 3{\cdot}7941 : 1 : 1{\cdot}1807$, $\beta = 105°48'$ (Groth, "Chemische Krystalographie", V, p. 34).

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* Thiantherene was kindly prepared for our use by Prof. P. C. Guha of the Indian Institute of Science, Bangalore, to whom our best thanks are due.

Plate IV
a—axis

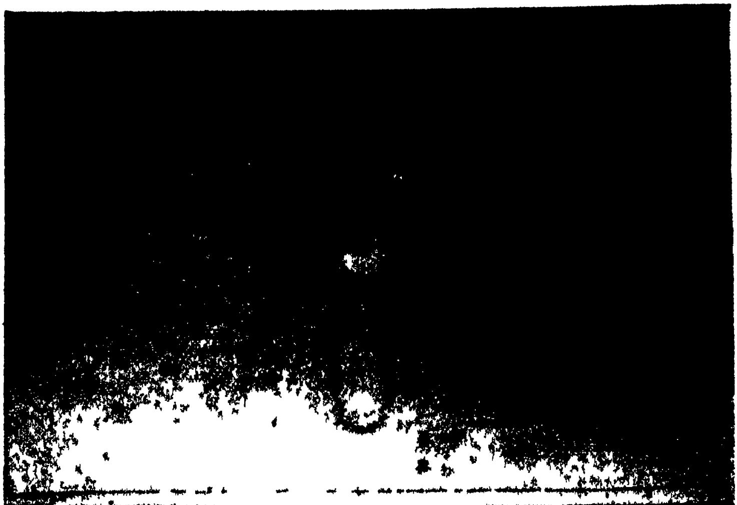
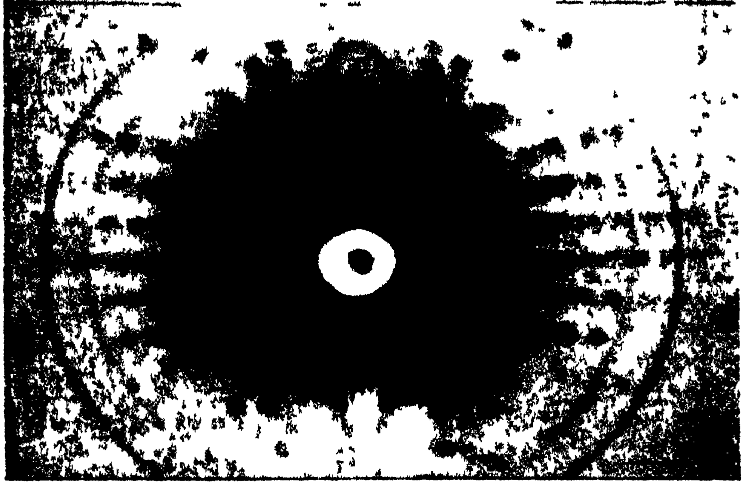


Plate II
b—axis

Plate III
c—axis



Rotation photograph of diphenyl disulphide

Plate IV
a—axis

Plate V
b—axis

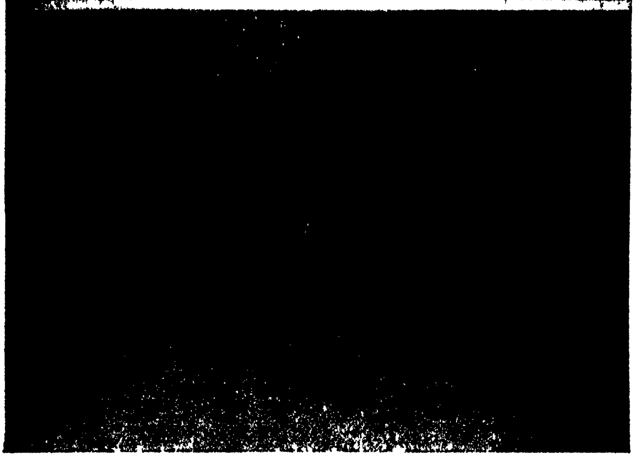


Plate VI
c—axis

Photographs.—The rotation photographs about a, b, and c-axis (Plates I, II, III) and several oscillation photographs at suitable intervals about each of the three axes, were taken. The dimensions of the unit cell are

$$a=23{\cdot}3\text{Å},\ b=6{\cdot}14\text{Å},\ c=14{\cdot}52\text{Å},\ \beta=105^\circ 51',$$

and the axial ratio is

$$a:b:c::3{\cdot}793:1:(2\times 1{\cdot}182)$$

which agrees with Groth's except that c/b is doubled. The angle β was directly measured from a number of crystals on all of which the (001) and the (100) faces were very well developed, and was found to be ($\beta=105^\circ 51$) the same as given by Groth.

The spots appearing on various oscillation photographs were indexed by the use of Bernal's chart. Tables I and II give the list of planes identified together with an approximate idea of their intensity for which the usual notations have been used.

TABLE I.

Axial planes.	Prism		planes	
	(hol)	$(ho\bar{l})$	(okl)	(hko)
002 v.s.	202 s.	$20\bar{2}$ m.s.	011 v.s.	210 s.
004 s.	204 m.	204 w.	013 s.	220 m.s.
006 m.s.	205 w.	—	014 s.	230 w.m.
008 m.	206 w.	$20\bar{6}$ w.	015 m.s.	320 m.
020 w.m.	207 v.w.	—	016 w.m.	330 m.
400 v.s.	--	401 m.s.	022 w.m.	410 w.m.
800 w.	402 s.	—	023 w.m.	430 w.m.
(10)00 w.m.	404 w.m.	$40\bar{4}$ m.	024 w.m.	510 m.s.
(12)00 w.	406 m.	$40\bar{6}$ w.m.	025 w.	520 w.m.
	601 w.	$60\bar{1}$ s.	026 w.	530 w.m.

TABLE I. (*contd.*).

Axial planes.	Prism	Planes.		
	(h0l)	(h0$\bar{l}$)	(0kl)	(hk0)
	602 w.	$60\bar{2}$ w.m.	031 w.m.	610 s.
	604 w.	$60\bar{4}$ m.s.	032 w.m.	620 w.m.
	605 w.m.	—	033 m.s	720 w.
	606 w.m.	—	034 m.	730 w.m.
	—	$80\bar{1}$ w.		810 w.m.
	802 w.m.	$80\bar{2}$ w.m.		820 w.m.
	804 w.m.	$80\bar{4}$ w.m.		910 w.m.
	—	$80\bar{6}$ w.m.		(10)10 w.m.
	—	$80\bar{7}$ w.		(10)20 w.
	—	$80\bar{8}$ w.m.		
	(10)02 w.m.	(10)$0\bar{2}$ w.		
	—	(10)$0\bar{4}$ w.		
	—	(10)$0\bar{5}$ v.w.		
	—	(10)$0\bar{6}$ m.s.		
	—	(12)$0\bar{4}$ w.		

TABLE II.

General planes.

111 s.	$11\bar{1}$ v.s.	215 w.	$21\bar{5}$ w.m.	—	$32\bar{4}$ w.m.
113 s.	$11\bar{3}$ s.	216 w.	$21\bar{6}$ w.	325 w.m.	$32\bar{5}$ w.m.
—	$11\bar{4}$ w.	—	$21\bar{7}$ m.	331 w.m.	$33\bar{1}$ w.
115 m.s.	$11\bar{5}$ m.s.	221 s.	$22\bar{1}$ m.s.	332 w.	$33\bar{2}$ w.m.
116 w.m.	$11\bar{6}$ w.m.	222 m.s.	$22\bar{2}$ m.	—	$33\bar{3}$ m.

TABLE II. (*contd.*).

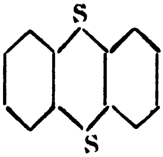
122w.m.	122w.m.	226w.	—	412s.	$41\bar{2}$s.
123w.m.	123w.	227v.w.	—	413w.	—
124w.m.	124w.	231m.	231w.m.	414w.	$41\bar{4}$w.
125w.	125w.	232w.	$23\bar{2}$w.	—	$41\bar{5}$w.
126w.	126w.	233w.m.	233w.m.	416w.m.	416w.
127v.w.	—	234m.	234m.s.	—	418w.m.
131w.m.	131w.m.	311s.	$31\bar{1}$m.s.	421m.s.	—
132w.m.	132w.m.	312w.	—	422m.s.	$42\bar{2}$m.s.
133m.	133w.m.	313w.	313w.m.	—	423w.m.
134m.	134m.	315w.m.	315w.m.	424w.m.	424w.m.
212v.w.	212s.	317w.m.	$31\bar{7}$m.	425w.m.	425w.m.
213s.	213s.	—	322m	431w.m.	$43\bar{1}$w.m.
214m.s.	214m.s.	323m.	323m.s.	432w.	—
—	$43\bar{3}$w.	—	$61\bar{8}$v.w.	—	821v.w.
434m.s.	$43\bar{4}$m.	621w m.	—	822w.	$82\bar{2}$w.
511s.	511v.s.	622w.m.	622w.m.	—	825w.m.
512m.	—	623w.	—	—	826w.m.
513w.m.	513w.m.	625m.s.	625m.	911m.s.	911m.s.
515m.	$51\bar{5}$m.s.	626w.	$62\bar{6}$w.m.	912w.m.	912m.
—	$51\bar{7}$m.	631w.m.	$63\bar{1}$w.m.	913m.	913m.
521w.m.	521m.	633w.	633w.m.	—	915w.
522w.m.	522m.	711w.m	$71\bar{1}$w.m	921w	921w.m.
523m.	$52\bar{3}$m.	713w.m.	713w.m.	—	922w.m.
525w.m.	525m.	715w.m.	715w.m.	925w.m.	925m.
—	526m.	—	717w.m.	—	(10)11w.m.
531m.	—	721w.m.	$72\bar{1}$w.m.	(10)12w.m.	(10)$\bar{1}$2w.
—	$53\bar{2}$w.m.	722w.	$72\bar{2}$w.m.	—	(10)$\bar{1}$4w.m.
533w.m.	—	723m.	$72\bar{3}$m.s.	(10)22w.m.	(10)$\bar{2}$2w.
534w.m.	$53\bar{4}$m.	725m.	725m.	—	(10)$\bar{2}$3w.
612s.	$61\bar{2}$m.s.	—	$72\bar{6}$w.	(10)24w.	(10)24w.m.
614w.m.	$61\bar{4}$ v.w.	811w.m.	$81\bar{1}$m.s.	—	(10)$\bar{2}$6w.

TABLE II. (*contd.*).

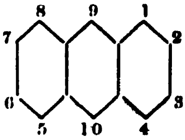
117m.s.	$1\bar{1}7$w.m.	224w.m.	$2\bar{2}4$w.	—	$33\bar{4}$w.
121v.s.	$1\bar{2}1$s.	—	225v.w.	326v.w.	—
615w.m.	—	812w.m.	$8\bar{1}2$w.m.	(11)11w.m.	(11)11w.
616v.w.	616w.m.	—	813m.	—	(11)12w.
—	$6\bar{1}7$w.m.	—	815w.m.	—	(11)13w.m.
—	$(1\bar{1})$ 15v.w.	—	(11)24w.	—	(12)13w.
(11)21w.	—	—	(11)25w.m.	—	(12)$1\bar{4}$w.
—	(11) $2\bar{2}$w.	—	(12)11w·m·	—	(13)13w.m.
—	(11) 23w.	—	(12)12w.		

The above tables show that (hol) planes are halved when *h* is odd and (010) is also halved. These halvings correspond to the space group C_{2h}^{5} ($P2_{1/n}$) with Γ_m Bravais lattice (Astbury and Yardly, *Phil. Trans.*, 1924, **A 224**, 230). The maximum number of asymmetric units required to complete the symmetry of this group is four. The number of molecules (mol. wt. 216) calculated from the observed data is eight (accurately 8·04).

The chemical molecule of thianthrene is represented as in (I). This representation resembles that of anthracene (II) in all respects excepting that the two carbon atoms in positions 9 and 10 in (II) are replaced by S atoms.



(I)



(II)

In the case of anthracene which also belongs to the space group C_{2h}^{5}, Bragg (*Proc. Phys. Soc.*, 1922; **34**, 33) has found that the calculated number of molecules per unit cell is only two, thus showing that the molecules are centro-symmetrical. In thianthrene, however, the results show that the number of molecules is double the number required by the unit cell. Such a result can only be explained by the assumption that two chemical molecules of thianthrene polymerise[*] to form an asymmetric unit of the elementary cell. The result appears surprising indeed looking to the high symmetry apparently exhibited by the chemical representation of the molecule. Cases of polymerisation taking place in the crystal unit, though rare, have been discovered by various workers from the results of *X*-ray analysis. Amongst the earliest examples, mention may be made of the results on phenylenediamines studied by Caspari (*Phil. Mag.*, 1927, **4**, 1276). Triphenylmethane studied by Prasad, deSousa and Jagdish (*J. Univ. Bombay*, 1936, **5**, 109) is another example of a similar nature. K. Baneriee has recently reported more such examples both in organic and inorganic compounds (*Proc. Indian Science Congress*, 1937).

Diphenyl Disulphide.

Eastman and Kodak's diphenyl disulphide was purified by recrystallisation from amyl acetate. The pure substance melted at 61° and the specific gravity was found to be 1·339. Well developed crystals were obtained by slow evaporation of a solution of the substance in acetone. The following table gives the interfacial angles.

TABLE III.

Interfacial angles of diphenyl disulphide.

Faces.	Groth's values		Authors' values	
	Calc.	Obs.	Calc.	Obs.
(110) : (1$\bar{1}$0)	68° 36′	—	68° 42′	68° 40′
(210) : (2$\bar{1}$0)	—	[†]37° 40′	37° 43′	—
(230) : (010)	44° 21′	[†]44 40′	44° 17′	—
(101) : (100)	—	[†]53° 50′	55° 9′	—
(101) : (210)	56° 3′	55° 47′	57° 16½′	—
(101) : ($\bar{1}$01)	72° 20′	—	69° 42′	70° 10′
(011) : (010)	63° 30′	64° 8′	64° 33′	—
(0$\bar{1}$1) : (011) .	53° 0′	—	50° 54′	52° 0′

---

[*] It may be mentioned here that cases of polymerisation known in organic chemistry are fundamentally different from the one dealt with here For example, acetaldehyde (CH_3CHO) polymerises to give paraldehyde, $(CH_3CHO)_3$, which has chemical and physical properties entirely different from the parent substance.

[†] The plane (230) given here is (340) mentioned by Groth (*loc. cit.*). This seems to be a misprint or an error.

The crystals belong to the orthorhombic system and the axial ratio is $a : b : c = 0{\cdot}6821 : 1 : 0{\cdot}4987$ (Groth, *loc. cit.*, p. 33).

Photographs.—The rotation photographs taken about the three crystallographic axes (Plates IV, V and VI) give the following dimensions of the unit cell

$$a = 8{\cdot}1\text{Å}, \qquad b = 23{\cdot}70\text{Å} \qquad c = 5{\cdot}64\text{Å}$$

and the axial ratio is

$$a : b : c = 0{\cdot}3418 : 1 : 0{\cdot}2380.$$

It will be seen that the b-axis is doubled in this case (*cf.* Groth, *loc. cit.*). The ratio $b : c$ obtained by the authors is slightly lower than that expected from Groth's value· However, Table III shows that the observed angles are in better agreement with those calculated from author's ratio. Tables IV and V give the list of planes identified on the oscillation photographs about the three crystallographic axes.

TABLE IV.

Axial planes.		Prism	planes.		
		(okl).	(hol).	(hko).	
002	m.	011 m.s.	101 m.s.	110 v.s.	2(11)0 v.w.
020	m.s.	012 m.	102 m.	120 m.	2(12)0 v.w.
040	w.m.	021 s.	201 m.s.	130 m.	310 m.
060	v.s.	023 w.	202 m.s.	140 m.	320 m.
080	m.s.	031 s.	301 m.	150 w.	330 w.
0(12)0	m.	032 w.m..	302 v.w.	160 m.	340 w.m.
200	s.	041 m.	401 w.	170 m.	350 m.
400	m.	042 w.	...	180 v.w.	360 w.m.
...		043 w.	...	190 m.	370 m.
...		051 m.	...	1(10)0 w.	380 w.
...		052 w.m.	...	1(11)0 w.m.	3(10)0 w.
...		061 m.	...	1(12)0 w.m.	410 w.m.
...		062 w.m.	...	210 m.	420 m.
...		063 w.	...	220 m.s.	430 w.m.
...		071 m.	...	230 m.	440 w.
...		072 w.m.	...	240 m.	450 m.
...		081 m.	...	250 v.w.	460 m.
...		091 w.m.	...	260 m.	470 w.
...		092 v.w.	...	270 w.	...
...		0(10)1 w.	...	280 w.	...
...		0(11)1 w.	...	...	...
...		0(12)1 w.	...	...	...

TABLE V.

General planes.

111 s.
112 m.s.
113 w.m.
121 m.s.
122 w.
123 w.
131 m.
132 w.m.
133 w.
141 w.m.
142 m.s
143 w
151 m.s.
152 w m.
153 v.w.
161 m.s
162 w.

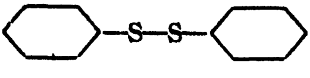
171 m.
172 w.m.
181 m.
182 w.m.
191 w.m.
192 w.
1(10)1 w.
1(10)2 w.m.
1(11)1 w.
1(12)1 w.m.
211 m.s.
212 w.
221 m.s
222 m.
231 m.s
232 m.s.
241 w.

242 w.
251 m.
252 w.m.
261 m.
262 w.
271 w.m.
281 w.m.
291 w.
292 v.w.
2(10)1 v.w.
2(11)1 w.m.
2(12)1 v.w.
311 m.
312 w.
321 m.
322 w.m.
331 m.s.

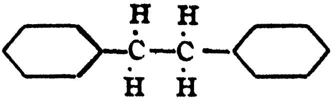
332 w.m.
341 w.
342 w.m.
351 w.
352 w.
361 m.
362 w.
371 w.
381 w.
391 v.w.
411 w.
421 w.m.
431 w
441 w.
451 w.
461 w.
...

From the above list of planes, it will be seen that planes (hoo), (oko), or (ool) are halved when h, k or l are, respectively, odd. The crystals, therefore, belong to the rhombic bisphenoidal class and to the space group Q^4 with Γ_0 Bravais lattice. The number of molecules calculated from the dimensions of the cell and specific gravity of crystals is four (accurately 4·005) which is the same as the maximum number of asymmetric units required to complete the symmetry of the space group Q^4. Thus it would seem that the molecules are asymmetric.

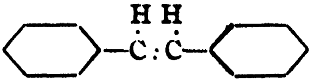
The chemical molecule of diphenyl disulphide is represented as in (III). From this representation the molecule appears to be similar to those of dibenzyl series (IV—VI).



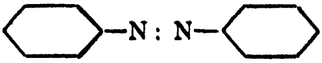
(III) Diphenyl disulphide.



(IV) Dibenzyl.



(V) Stilbene



(VI) Azobenzene.

Now, in the case of dibenzyl, Dhar (*loc. cit.*) has shown that the number of molecules is half the number of asymmetric units required by the space group. This is indicative of a centre of symmetry in dibenzyl. In the case of stilbene and azobenzene also Robertson, Prasad and Woodward (*loc. cit.*) have shown that the molecules are centro-symmetrical although the calculated number of molecules is the same as the number required to complete the symmetry of the cell.

From this it appears that the possibility of molecules of diphenyl disulphide possessing a centre of symmetry is not entirely to be excluded.

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PROPERTIES OF ACTIVATED SUGAR CHARCOAL COATED WITH VARIOUS ORGANIC SUBSTANCES. PART II. ADSORPTION OF ACIDS.

By Harendra Kumar Acharya.

In a previous paper (Acharya, *J Indian Chem. Soc.*, 1936, **13**, 723) a method has been described of depositing acidic and alkaline coats on the surface of activated sugar charcoal. The relation between such coats and the adsorption of acids has been investigated in the present paper.

It appears that centres with basic or acidic properties should adsorb respectively acids or bases. The adsorption of benzoic acid by activated sugar charcoal, was chosen as an index to changes in the acid adsorbing properties. It appears that a distinction should be made between a direct adsorption of acids or bases by carbon atoms on the surface, and an indirect or secondary adsorption through the already adsorbed basic or acidic molecules or groups respectively which are present on the surface.

In discussing the results obtained in this paper it is necessary to obtain some estimate of the specific surface (*i. e.*, area of surface per gram) of the charcoal. The estimates of different authors vary widely from 0·9 to 1000 sq. metres (Lamb, Wilson and Chaney, *Ind. Eng. Chem.*, 1919, **11**, 420; Williams, *Proc. Roy. Soc.*, 1919, **A96**, 287; Lowry and Hulett, *J. Amer. Chem. Soc.*, 1920, **42**, 1393; Ruff, Ebert and Luft, *Z. anorg. Chem.*, 1928, **170**, 49; Marshall and Bramston-Cook, *J. Amer. Chem. Soc.*, 1929, **51**, 2019). The specific surface is generally calculated from the adsorption isotherms of suitable substances. The value thus obtained depends, however, on the choice of the adsorbates. Thus Paneth and Radu (*Ber.*, 1924, **57B**, 1221) found that areas per g. of a sample of charcoal range from 46·2—268 sq. metres for different absorbates. The estimations of Lowry (*J. Phys. Chem.*, 1930, **34**, 63), according to which the surface of 23 samples of charcoal ranged from 0·9—32·2 sq. metres, will be used for the discussion of the results given in this paper.

EXPERIMENTAL.

The sugar charcoal used in the following experiments was obtained by activating pure sugar charcoal at 800° for six hours in air at a pressure of

1 mm. The resulting charcoal had a small negative charge in contact with water. The coatings were produced as follows:

5 G. of the charcoal were kept for 24 hours in contact with 10 c.c. of an alcoholic solution containing a definite amount of the organic substance. The alcohol was next evaporated and the charcoal dried in a silica crucible on a water-bath.

For the adsorption experiments, 50 c. c. of the acid solutious and 0·5 g. of the charcoal were used in each case. After 24 hours the supernatant liquids were separated by a powerful centrifuge and titrated against standard solutions of baryta using phenolphthalein as the indicator.

TABLE I.

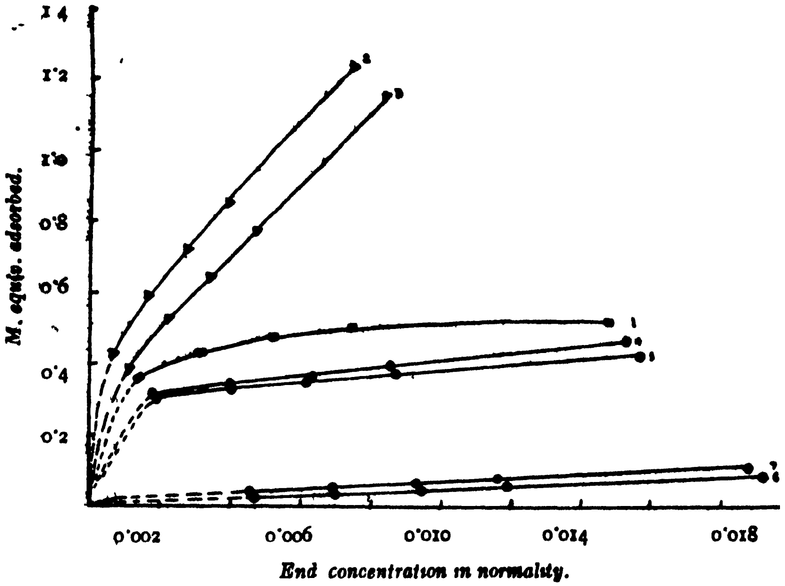
Adsorption of benzoic acid.

Amount of the substance per g. of charcoal.	Concentration of the acid		Amount adsorbed (m. equiv. per g. of charcoal).
	Initial.	End.	
Original activated charcoal. (*cf*. curve 1)	0·02 *N*	0·01476 *N*	0.524
	0·0125	0·00745	0·505
	0 01	0·00520	0·480
	0·0075	0·00315	0·435
	0·005	0·00137	0·363
0·01 G. of α-naphthylamine (*cf*. curve 2)	0·02	0·00761	1·239
	0·0125	0·00394	0·856
	0·01	0·00275	0·725
	0·0075	0·00154	0·596
	0·005	0·00068	0·432
0·01 G. of diphenylamine (*cf*. curve 3)	0·02	0·00845	1·255
	0·0125	0·00474	0·776
	0·01	0·00347	0·658
	0·0075	0·00221	0·529
	0·005	0·00110	0·390

Amount of the substance per g. of charcoal.	Concentration of the acid Initial.	End.	Amount absorbed (m. equiv. per g. of charcoal).
0·01G. of lauric acid (*cf* curve 4)	0·02	0·01530	0·470
	0·0125	[illegible]	0·395
	0·01	0·00630	0·370
	0·0075	0·00402	0·348
	0·005	0·00179	[illegible]
0·01G. of myristic acid (*cf.* curve 5)	0·02	0·01568	0·432
	0·0125	0·00870	0·380
	0·01	0·00640	0·360
	0·0075	0·00408	0·342
	0·005	0·00185	0·315
0·01 G. of palmitic acid (*cf.* curve 6)	0·02	0·01921	0·079
	0·0125	0·01188	0·062
	0·01	0·00947	0·053
	0·0075	0·00702	0·048
	0·005	0·00465	0·035
0·01 G. of stearic acid (*cf.* curve 7)	0·02	0·01890	0·110
	0·0125	0·01168	0·082
	0·01	0·00932	0·068
	0·0075	0·00694	0·056
	0·005	0·00456	0·044

Table I shows that the amine coats increase the adsorption of benzoic acid by more than 100%, α-naphthylamine coat being more effective than that of diphenylamine (Fig. 1, curves 1, 2 and 3). On the other hand coats with different acids diminish the adsorption of the same to different extents, the order being palmitic acid > stearic acid > myristic acid ≥ lauric acid (Fig. 1, curves 4, 5, 6 and 7).

FIG. 1.



Curves 1–7 refer respectively to original charcoal, and charcoal coated with α-naphthylamine, diphenylamine, lauric, myristic, palmitic and stearic acids.

The following results show that the interaction between the pure amine and benzoic acid cannot account for the increase in adsorption of benzoic acid. The charcoal surface thus plays a definite rôle in this respect. 0·005 G. of α-naphthylamine was shaken with 50 c. c. of the benzoic acid solution of different concentrations.

TABLE II.

Concentration of the acid Initial.	 End.	Amount adsorbed (m. equiv. per g. of charcoal).
0·02*N*	0·02*N*	Nil
0·0125	0·0125	"
0·01	0·01	"
0·0075	0·0075	"
0·005	0·005	"

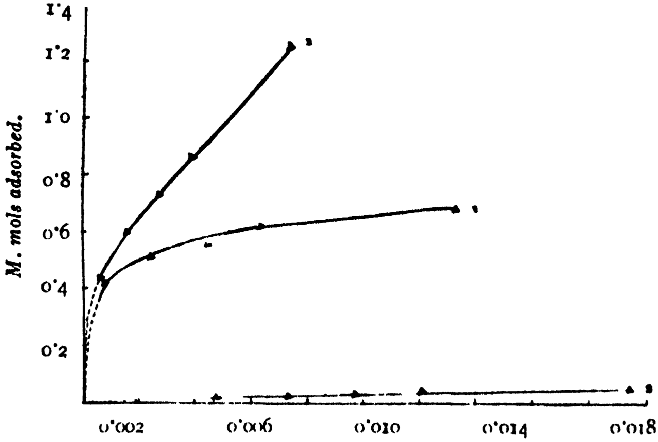
The spreading of the amine molecules on the charcoal surface would expose them to possible interactions, and the amine molecules are probably linked to the surface atoms by chemical valences, and orientation perhaps intensify their capacity to react with acid molecules. In the latter case, we should expect a maximum adsorption of benzoic acid when the whole charcoal surface is covered with a monomolecular layer of the amine. The adsorption of benzoic acid thus passes through a peak value as shown in Table III.

TABLE III.

Amount of the substance per g. of charcoal.	Concentration of the acid Initial.	End.	Amount adsorbed (m. equiv. per g. of charcoal).
0·005 G. of α-naphthylamine (*cf.* curve 8)	0·02*N*	0·01340*N*	0·660
	0·0125	0·00640	0·610
	0·01	0·00450	0·550
	0·0075	0·00246	0·504
	0·005	0·00074	0·426
0·01 G. of α-naphthylamine (*cf.* curve 2)	0·02	0·00761	1·239
	0·0125	0·00394	0·856
	0·01	0·00275	0·725
	0·0075	0·00154	0·596
	0·005	0·00068	0·432
0·05 G. of α-naphthylamine (curve 9)	0·02	0·01950	0·050
	0·0125	0·01210	0·040
	0.01	0·00968	0·032
	0·0075	0·00729	0·021
	0·005	0·00483	0·017

With 0·05 g. of the amine per g. of charcoal, the adsorptive capacity of the charcoal is almost negligible, while with 0·005 g. of the same an isotherm curve with greater adsorption than the original charcoal is obtained. The maximum adsorption of the acid (0·02*N*) occurs with 0·01 g. of the amine per g. of charcoal, being above 135% greater than that on the original (uncoated) charcoal (Fig. 2, curves 2, 8 and 9).

FIG. 2.



Curves 2, 8 and 9 refer respectively to 0·01g., 0·005 g. and 0·05 g. of α-naphthylamine.

The maximum adsorption of benzoic acid by 'coated' charcoal is 1·239 m. equiv. Schroder (*Ber.*, 1879, **12**, 562) finds the density of benzoic acid to be 1·292. Assuming the molecules to be cubes and to be spread as a continuous unimolecular layer, the above value of the maximum adsorption gives the specific area of the covered surface to be 288 sq. meters. The same method of calculation gives 101 sq. metres as the specific surface of the charcoal before the coating was applied. This value corresponds to the maximum adsorption 0·524 m. equiv. (*cf.* Fig. 1, curve 1).

Approximate values of the areas, which can be covered by a unimolecular film of the substances forming the coats, are given in Table IV. The cross section of the molecules, calculated by Adam (*Proc. Roy. Soc.*, 1922, **A101**, 452) from surface pressure measurements and the density data of the amines (Dunstan, *J. Chem Soc.*, 1915, **107**, 668), have been used for this purpose.

TABLE IV.

Substance.	Amount per g. of charcoal.	Cross-section in Sq. Å.	Density.	Approximate area in sq. metres.
Lauric acid	0·01	20·5	—	6·21
Myristic acid	,,	,,	—	5·55
Palmitic acid	,,	,,	—	4·96
Stearic acid	,,	,,	—	4·35
Diphenylamine	,,	—	$1{\cdot}162^{20^\circ}_{4}$	16·71
α-Naphthylamine	0·001	—	$1{\cdot}171^{20^\circ}_{4}$	1·77
	0·005	—	,,	8·83
	0·01	—	,,	17·66
	0·05	—	,,	88·30

If we consider Lowry's (*loc. cit*) limiting value (32·2 sq. meters) as the area for the present sample of charcoal, the different amounts of the coating substances, if spread unimolecularly, appear to be insufficient to cover the whole surface, while the maximum quantity of α-naphthylamine used for the coat (0·05 g.) may cover the total charcoal surface and form more than two layers. But the surface as calculated from the adsorption isotherm of benzoic acid on the original charcoal is 101 sq. metres. If this latter value is taken to be more reliable then it is necessary to conclude that the surface is not fully coated when the adsorption is totally stopped. It is necessary to point out that the method of producing the coat entails the possibility that the coating substances cover the exterior surface of the granules and prevent an ingress of the adsorbate to the internal surfaces.

It is, however, difficult to explain the larger adsorption of benzoic acid. 0·01 G. of amine would contain $4 \cdot 24 \times 10^{19}$ molecules, whereas one g. of the charcoal, coated with this amount of the amine, shows an increase in adsorption of $4 \cdot 33 \times 10^{20}$ molecules of benzoic acid. It is evident that the amine groups on the surface are not the only places where single molecules of benzoic acid are adsorbed. One has to assume that either each amine group on the surface adsorbs more than one molecule of benzoic acid or the coating material increases the active surface where benzoic acid is adsorbed.

With a view to confirm the above results with benzoic acid, the adsorption of salicylic, succinic and oxalic acids was also carried out at one concentration, *viz.*, 0·01*N*. The results are given in Tables V, VI and VII.

TABLE V.

Adsorption of salicylic acid.

Amount of the substance per g. of charcoal		End. conc. of the acid.	Amount adsorbed (m. equiv. per g. of charcoal).
Original charcoal		0·00636*N*	0·364
0·01 G. of	lauric acid	0·00766	0·234
„	myristic acid	0·00782	0·218
„	palmitic acid	0·01	Nil
„	stearic acid	0·00979	0·021
„	diphenylamine	0·00613	0·387
0·001	α-naphthylamine	0·00608	0·392
0·005	„	0·00536	0·464
0·01	„	0·00593	0·407
0·05	„	0·01	Nil

TABLE VI.

Adsorption of succinic acid.

Amount of the substance per g. of charcoal.		End. conc. of the acid.	Amount absorbed (m. equiv. per g. of charcoal).
Original charcoal		0·0068 N	0·340
0·01 G. of	lauric acid	0·00774	0·226
„	myristic acid	0·00782	0·218
„	palmitic acid	0·00971	0·029
„	stearic acid	0·00966	0·034
„	diphenylamine	0·00638	0·632
0·001	α-naphthylamine	0·00649	0·351
0·005	„	0·00570	0·430
0·01	„	0·00585	0·415
0·05	„	0·00997	Nil

TABLE VII.

Adsorption of oxalic acid.

Ammount of the substance per g. of charcoal.		End conc. of the acid.	Amount adsorbed (m. equiv, per g. of charcoal).
Original charcoal		0·00836N	0·164
0·01 G. of	lauric acid	0·00859	0·141
„	myristic acid	0·00882	0·118
„	palmitic acid	0·00996	Nil
„	stearic acid	0·00971	0·029
„	diphenylamine	0·00802	0·198
0·001	α-naphthylamine	0·00809	0·191
0·005	„	0·00764	0·236
0·01	„	0·00787	0·213
0·05	„	0·00989	Nil

The results in Tables V, VI and VII are quite in agreement with those obtained with benzoic acid. The different acid coats, perhaps act as a poison towards the adsorption of the acids to different extents. The adsorption of the acids on the other hand is increased with increasing amount of the amine coat and appears to pass through a maximum; further when the amount of the coat is sufficiently increased, the adsorption is totally stopped. The maximum increase in adsorption with the amine coat, which occurs when 0·005 g. of α-naphthylamine is spread per g. of charcoal, is about 25% with salicylic acid, 25% with succinic acid and 40% with oxalic acid.

The decrease in the adsorption of the acids in contact with the charcoal, coated with different acids, may be expected to be the result of some of the acid coat coming out into the solution and increasing the titratable acid. But it has been shown in Part I of this series (*loc. cit.*) that the p_H values of conductivity water, kept in contact for 24 hours with the above coats, are never less than 5. The solubility of the coats has thus little to do with the decrease in adsorption.

SUMMARY.

1. Coats of various organic substances, such as lauric, myristic, palmitic and stearic acids and α-naphthyl and diphenylamines have been produced on activated sugar charcoal and the influence of such coats on the adsorption of benzoic, salicylic, succinic and oxalic acids by charcoal has been studied.

2. The amine coats greatly increase the adsorption of the acids, an α-naphthylamine coat being more effective than that of diphenylamine. This increase reaches a maximum as the amount of the amine used for coating the charcoal is increased, but with further increase, the adsorption decreases to zero. The maximum increment in the adsorption of benzoic acid (0·02N) which has been observed is more than 135%, and occurs with 0·01 g. of α-naphthylamine per g. of charcoal. The maximum adsorption of salicylic, succinic and oxalic acids (0·01 *N*) occurs with 0·005 g. of the amine and is of the order of 25% to 45%. The maximum adsorption of benzoic acid, assuming that the adsorbed molecules are spread unimolecularly on the surface, gives a value of 288 sq. meters for the specific surface.

3. The different acid coats, on the other hand, decrease the adsorption of the acids to different extents. The capacity of the coats to diminish the adsorption of the acids is of the order: palmitic acid > stearic acid > myristic acid > lauric acid.

My best thanks are due to Prof. J. N. Mukherjee for his advice and facilities for this work.

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ON THE STUDY OF POLYHALIDES. PART V. THE STRUCTURE OF POLYHALIDES.

BY SUSIL KUMAR RAY AND DURGADAS MAJUMDAR.

Inspite of investigations extending over a period of more than a century the constitution of the polyhalides is still a matter of much controversy. Attempts at elucidating the structure of these compounds have not as yet been very successful nor has any systematic investigation been made in this direction.

By studying the reactions of *para*-bromophenyltrimethylammonium trihalides, Reade (*J. Chem. Soc.*, 1923, **123**, 141 ; 1924, **125**, 148 ; 1926, 2528) proposed the following structure for the trihalides :

$$Q_m\,[\bar{X}_1-\overset{+}{X}_2-\bar{X}_3]$$

where Q_m stands for the organic cation and X_1, X_2, X_3 for the halogen atoms which may be all different or two similar and one different.

From studies in absorption band spectra Lowry and Sass (*ibid.*, 1926, 622) have confirmed the observations of Crymble, Stewart and Wright (*Ber.*, 1910, **43**, 1183) that KI_3 and CHI_3 have similar absorption band. No similarity is exhibited by any of the conventional formulæ for the polyhalides and iodoform, the most plausible structure for the former being that given by Reade. Further studies in the absorption spectra of the polyhalides by Goldstein and Lowry (*J. Chem. Soc.*, 1931, 1092) have led these authors to confirm the structure given by Reade (*loc. cit.*).

Ray (*J. Indian Chem. Soc.*, 1933, **10**, 213 ; 1934, **11**, 115) from observations of the variations in the equilibrium constant of reactions

$$RX+X_2 \rightleftharpoons RX_3$$

(where R stands for H, Na, K, etc., and X stands for a halogen) suggested the structure of a trihalide to be

$$R\,[\bar{X}_1(\overset{+-}{X}_2)]$$

where X_1 stands for the halogen ion and X_2 for the halogen molecule. According to Ray (*loc. cit.*) the union between the halogen ion and the halogen molecule is of an electrostatic nature. This structure, it will be observed, has some similarity to that suggested by Reade.

The first attempt to explain the structure from the standpoint of the electronic theory of valency was made by Gray and Dakers (*Phil. Mag.*, 1931, **11**, 81). They have measured the diamagnetic susceptibilities of the tetraalkylammonium polyhalides, prepared by Chattaway and Hoyle (*J. Chem. Soc.*, 1923, **123**, 654) and of the phenyltrimethylammonium polyhalides, prepared by Reade (*loc. cit.*). On the evidence of their observation, Gray and Dakers adopted the co-ordination theory of Werner and hence gave the structure,

$$:\underset{\cdot\cdot}{\ddot{\mathrm{M}}}:\,:\underset{\cdot\cdot}{\ddot{\mathrm{X}}}\;:\underset{\cdot\cdot}{\ddot{\mathrm{X}}}:\,:\underset{\cdot\cdot}{\ddot{\mathrm{X}}}:$$

for the trihalide, where M stands for a cation and X for any halogen excepting fluorine.

The possibility of the presence of single electron linkages in the polyhalide molecule was suggested by Cremer and Duncan (*J. Chem. Soc.*, 1933, 181) but no experimental evidence was given by these authors. The provisional structure of Cremer and Duncan should be

$$:\ddot{\mathrm{M}}:\,:\ddot{\mathrm{X}}\cdot\quad\dddot{\mathrm{X}}\cdot\,\dddot{\mathrm{X}}\cdot$$

where M stands for the cation and X for any halogen.

From the investigations on the structure of the polyhalides it will be observed that up till now only two structures have been given from the standpoint of the electronic theory of valency. The one suggested by Gray and Dakers (*loc. cit.*) assumes that the halogen atoms are linked together by election-pair bonds or normal co-valency, while the other put forward by Cremer and Duncan (*loc. cit.*) assumes that the bonds are single electron bonds. The object of the present paper is to decide between the structures proposed by Gray and Dakers and by Cremer and Duncan and to attempt to derive a structure of the polyhalides based on the Quantum mechanical theory of homopolar valency of Heitler and London. Since the single electron linkage hypothesis was put forward by Sugden from parachor studies, the determination of the parachor of the polyhalides will be the best method for deciding whether such linkages are present or not, and in the present paper this method has been resorted to. As the polyhalides studied decompose on fusion, Sugden's original method for the determination of the parachor of solid substances is not applicable here and hence the surface tension and density were determined in solution and the parachor calculated (Ray, *J. Indian Chem. Soc.*, 1934, **11**, 672, 843; 1935, **12**, 248, 404).

The polyhalides of the alkali metals of lower atomic weight are known in solution in the form of equilibrium mixtures and they can not be isolated in the pure state, while the polyhalides of the alkali metals of higher atomic weights will not be soluble in organic solvents and in aqueous solution they would most likely dissociate into ions. Moreover, the atomic parachor of the alkali metals are not reliable. So in the present paper the polyhalides of the substituted ammonium radical have been investigated which have the advantages of being stable at the ordinary temperature and also soluble in non-dissociating organic solvents.

Since the parachor is affected widely by association or dissociation, it is necessary to ascertain that such disturbing effects are not occurring. This has been done by the determination of the molecular weights of the substances by the freezing point method.

EXPERIMENTAL.

Preparations.

The compounds were prepared either according to the method of Reade or of Chattaway and Hoyle. Since the presence of slight impurities affect the surface tension widely, it is necessary that the substances should be in a high state of purity. The final compound as well as the intermediate compounds were repeatedly crystallised till a constant melting point was attained. One new compound was prepared in course of this investigation, its molecular formula was established by analysis and determination of molecular weight; its parachor was also determined. The following is the list of compounds prepared and studied.

(*i*) *Tetraethylammonium Tri-iodide* was crystallised from boiling alcohol till the constant melting point of 142° reached (Chattaway and Hoyle, m.p. 142°).

(*ii*) *Tetraethylammonium Iododibromide*, after three crystallisations from alcohol had a constant m.p. at 125° (Chattaway and Hoyle, m.p., 125°; Gray and Dakers, m.p. 124°).

((*iii*) p-*Bromophenyltrimethylammonium Iododichloride*, after three crystallisations from glacial acetic acid, had a constant m.p. at 178° (Reade, m.p. 177°).

(*iv*) p-*Bromophenyltrimethylammonium Iodotetrachloride*, crystallised from glacial acetic acid, had m.p. 190° (Reade, m.p. 188-89°).

(v) p-*Bromophenyltrimethylammonium Tribromide* crystallised from glacial acetic acid below 80°, m.p., 175° (Reade, m.p. 175°).

(vi) *Tetraethylammonium Iodobromotrichloride.*—Pure iodine (6 g.) was suspended in glacial acetic acid (10 c.c.) in a small flask cooled to about 15° and into this was passed pure and dry chlorine gas. The passage of chlorine was continued till crystals of iodine trichloride separated. The current of chlorine was then stopped and the supernatant liquid decanted off. Tetraethylammonium bromide (9 g.), crystallised from water was suspended in acetic acid and was added to the precipitate of iodine trichloride. The mixture was warmed on the water-bath to 80° and acetic acid added little by little till all solid matter dissolved. The solution on cooling yielded yellow crystals of tetraethylammonium iodobromotrichloride which were thrice recrystallised from glacial acetic acid when it had the constant m.p. of 171°. The substance is insoluble in water but fairly soluble in alcohol, nitrobenzene and acetic acid. It decomposes in pyridine. [0·2144 g. gave 0·4206 g. of silver halides; $N(C_2H_5)_4IBrCl_3$ requires 0·4136 g.] [Found: N, 2·98. $N(Et_4)IBrCl_3$ requires 3·15 per cent].

(vii) *Tetramethylammonium Pentaiodide* crystallised from alcohol, m.p. 130° (Chattaway and Hoyle, m.p. 130°).

Determination of Molecular Weight.

From the existing literature, it appears that the molecular weights of the polyhalides have not been determined. The usual method of establishing the formation of a definite compound in this line was by analysis of the compounds and seeing whether they fitted in the law of multiple proportions This method leaves the question open that the substances might be eutectic mixtures. A determination of the molecular weights of these compounds will settle this point, as eutectic mixtures can not give results corresponding to normal molecular weight; the cryoscopic method for the determination of molecular weights has been adopted. The solubility of the polyhalides in the usual solvents is not very great and it was found that they were in general moderately soluble in nitrobenzene (*vide* Nernst, " Theoretical Chemistry," English Translation by L.W. Codd, p, 167). In the present investigation nitrobenzene, purified by repeated distillation, was employed as the solvent.

A Beckmann thermometer graduated to 1/100th of degree was used. The temperature of the bath was kept only one degree below the freezing point of the solution. By careful stirring the supercooling of the solution was never allowed to exceed 0·1°. The results are tabulated in Table I.

TABLE I.

Compound.	Wt. in 100 g. of nitrobenzene.	Depression of freezing point.		M.W. (obs.)	M.W. (calc.)
NEt_4I_3	0·9756	0·135		511	
	1·9780	0·275		508·6	
	2·5046	0·350		505·9	
			Mean	508·5	511
NEt_4IBr_2	0·9854	0·170		409·9	
	1·9805	0·340		411·7	
	2·5046	0·425		416·7	
			Mean	412·7	417
$C_6H_4Br{\cdot}NMe_3ICl_2$	0·9232	0·160		408·0	
	1·8500	0·315		415·3	
	3·6021	0·625		407·4	
			Mean	410·2	413·0
$C_6H_4Br{\cdot}NMe_3ICl_4$	0·8954	0·135		468·9	
	1·7810	0·265		475·2	
	2·3259	0·340		483·7	
			Mean	475·9	484·0
$C_6H_4Br.NMe_3Br_3$	0·5672	0·090		445·7	
	1·8070	0·285		448·3	
	2·2590	0.355		449·9	
			Mean	448·0	455·0
NEt_4IBrCl_3	1·1210	0·180		440.2	
	3·5160	0·565		439·9	
	4·3981	0·705		441·1	
			Mean	440·4	443·5
NMe_4I_5	1·252	0·175		505·8	
	2·593	0·400		458·2	
	3·125	0·595		368·5	709·0

Thus, with the exception of NMe_4I_5, which apparently decomposes, the molecular weights of the other compounds obtained experimentally agree closely with that calculated from analytical data.

Determination of Parachor.

The parachor of the above mentioned compounds were determined in solution by the method of Ray (*loc. cit.*). The first, second and the last compound were found to be very soluble in pyridine and so parachor determination of these compounds have been carried out in pyridine. With the exception of the sixth compound, which decomposes in pyridine and has therefore been investigated in nitrobenzene, the solubility of the other compounds was higher in nitrobenzene than in pyridine, and as such have been investigated in nitrobenzene. Pyridine used in this investigation was purified by distillation and then stored over pure caustic potash sticks in a stoppered bottle. Nitrobenzene was also similarly purified and then stored over pure fused calcium chloride. Dry and powdered substances whose parachor was to be determined were taken in 25 c.c. measuring flask (previously weighed emty and dry) and the total weight determined. The substance was dissolved in corresponding solvent and the weight of the solution determined. From these weighings the molar fraction of the solute was directly obtained.

The surface tension was determined by the maximum bubble pressure method. Altogether five to seven readings were taken on the manometer and the mean of all these readings was used in the calculation of the surface tension. The densities of the solutions were measured by means of a 10 c.c. stoppered pyknometer. The results are tabulated in Tables II-VIII. In these tables P_{pair} represents the value of the parachor calculated on the basis that the bonds between the halogen atoms are electron-pair bonds or normal co-valency, while P_{single} is the value calculated on the basis that the bonds are single electron linkages. In the following tables x is the mol. fraction of the solute, M_m, the mean molecular weight of the solution, P_m, the parachor of the solution, P_x, the parachor of the solute, d, the density and σ, the surface tension.

TABLE II.

Tetraethylammonium tri-iodide in pyridine.

x.	d.	σ.	M_m.	P_m.	P_x.	P_{pair}.	P_{single}.
0·0	0·9696	34·69	79·00	197·7	...	...	...
0·008574	1·002	35·65	82·70	201·7	664·8	...	...
0·008696	1·003	35·81	82·74	201·8	666·8	...	...
0·01123	1·015	36·44	83·86	203·0	667·9	...	...
0·01265	1·015	35·79	84·46	203·5	656·1	...	...
0·01493	1·027	36·78	85.43	204·8	676·4	..	...
0·01763	1·033	35·45	86·61	206·0	669·4	...	...
0·01858	1·041	37·12	87·03	206·4	667·4	...	...
				Mean	666·9	664·3	641·1

TABLE III.

Tetraethylammonium iododibromide in pyridine.

x.	d.	σ.	M_m	P_m	P_x.	P_{pair}.	P_{single}.
0·0	0·9696	34·69	79·00	197·7	...	...	...
0·01169	1·003	36·04	82·94	202·6	615·9	...	...
0·01255	1·007	36·31	83·23	202·9	613·7	...	...
0·01963	1·023	36·49	85·63	205·8	611·3	...	...
0·02371	1·030	36·45	87·00	207·5	611·6	...	..
0·02489	1·034	36·85	87·40	208·3	622·6	...	...
0·03230	1·050	36·93	89·90	211·1	613·1	...	...
				Mean	614·8	618·3	595·1

TABLE IV.

p-*Bromophenyltrimethylammonium iododichloride in* PhNO$_2$.

x.	d.	σ.	M_m.	P_m.	P_x.	P_{pair}.	P_{single}.
0·0	1·198	44·30	123·0	264·9	...	...	...
0·004573	1·207	44·70	124·4	266·5	612·4	...	...
0·004594	1·206	44·54	124·4	266·5	609·5	...	...
0·006451	1·208	44·50	124·9	267·1	620·0	...	...
0·007158	1·208	44·40	125·1	267·4	628·7	...	...
0·008682	1·214	45·16	125·5	268·0	622·0	...	...
0·009464	1·214	44·82	125·7	268·2	622·0	...	...
0·009574	1·211	44·42	125·8	268·2	616·3	...	...
				Mean	618·7	619·7	596·5

TABLE V.

p-Bromophenyltrimethylammonium iodotetrachloride in $PhNO_2$.

x.	d.	σ.	M_m.	P_m.	P_x.	P_{pair}.	P_{single}.
0·0	1·198	44·30	123·0	264·9	...	...	...
0.002952	1·206	44·79	124·1	266·2	711·2	...	...
0·003639	1·207	44·75	124·4	266·6	714·5	...	...
0·006551	1·211	44·80	125·4	267·9	732·6	...	...
0·006736	1·214	45·20	125·5	268·1	742·3	...	...
0·008175	1·214	44·87	126·0	268·6	721·8	...	...
				Mean	724·4	728·3	693·5

TABLE VI.

Tetraethylammonium iodobromotrichloride in $PhNO_2$.

x.	d.	σ.	M_m.	P_m.	P_x.	P_{pair}.	P_{single}.
0·0	1·198	44·30	123·0	264·9	...	...	..
0.009665	1·203	43·48	126·1	269·2	713·9	...	...
0·01206	1·208	44·00	126·8	270·4	721·4	...	...
0·01592	1·213	43·89	128·2	272·0	709·8	...	...
0·01786	1·215	44·01	128·7	272·9	716·6	...	...
0·01984	1·218	44·01	129·4	273·7	710·8	...	...
				Mean	714·5	713·2	678·4

TABLE VII.

p-Bromophenyltrimethylammonium tribromide in $PhNO_2$.

x.	d.	σ.	M_m.	P_m.	P_x.	P_{pair}.	P_{single}.
0·0	1·198	44·30	123·0	264·9	—		
0·004054	1·199	43·53	124·3	266·3	616·6		
0·004862	1·201	43·65	124·6	266·7	637·7		
0·005064	1·201	43·73	124·7	266·8	631·9		
0·006068	1·204	43·61	125·1	267·0	625·2		
				Mean	628·1	624·1	600·9

Table VIII.

Tetraethylammonium pentaiodide in pyridine.

x.	d.	σ.	M_m.	P_m.	P_x.	P_{pair}.	P_{single}.
0·0	0·9696	34·69	79·00	197·7	—		
0·004619	1·001	36·23	81·90	200·8	866·2		
0·006060	1·010	32·96	82·82	196·4	—		
0·007109	1·021	38·23	83·47	203·3	984·7		
0·008390	1·022	31·76	84 29	195·8	—		
0·01361	1·042	38·15	87·58	208·8	1014·0		
				Mean	—	691·9	645·5

DISCUSSION.

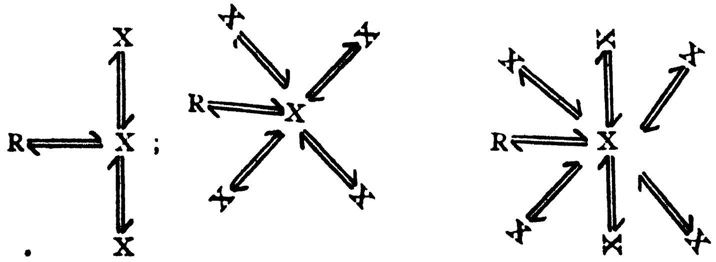
From the preceding tables it will be seen that the parachor values of the compounds obtained experimentally agree very closely to the value calculated on the assumption that the bonds between the halogens are electron-pair bonds. In the case of tetraethylammonium pentaiodide the data obtained (Table VIII) will show that the values are far from being constant. The determination of the molecular weight showed that the substance decomposes in solution and the erratic nature of the parachor values is apparently due to this decomposition. The investigation of the magnetic susceptibilities of this compound by Gray and Dakers (*loc. cit.*) did not tally with their theory. It may also be mentioned here that according to Ephraim (" Text Book of Inorganic Chemistry ", English Ed., 1934, p. 217) polyiodides higher than tri-iodides do not exist. The alleged higher iodides are solid solutions of iodine in tri-iodide and probably eutectic mixtures.

While the parachor values show that the bonds between the halogens are electron-pair bonds, corresponding structures can not be given from the classical electronic theory of valency of Lewis and Kossel. An attempt will be made to derive a structure of the polyhalides based on the quantum mechanical theory of Heitler and London. London (*Z. Physik*, 1928, **46**, 455) in extending this theory put forward that the variable valency of elements can be explained by supposing that the electron configuration of the atom varies from compound to compound so that the number of electrons with unpaired spins varies; the limitation to such variation being given by the exclusion rule of Pauli. The halogen atoms have the structure $n\,s^2p^5$, of the valency shell, where n stands for 2,3,4 or 5 in the cases of fluorine, chlorine, bromine or iodine. Corresponding to these structures there can be only one electron with unpaired spin in the atom and as such the halogens are monovalent in most of the compounds. Except fluoride all other halogens exhibit polyvalency. To explain this London assumes that the following electron configurations are possible without violating Pauli's rule, *viz.*,

$$ns^2p^4d,\ ns^2p^3d^2,\ nsp^3d^3$$

where n stands for 3,4 or 5 corresponding to chlorine, bromine or iodine. In the case of fluorine no other structure is possible without violating Pauli's rule and hence fluorine is consistently monovalent. Corresponding to the first, second or third of the structures suggested by London, the halogens can be tri-, penta- or heptavalent.

As has been already pointed out that Werner and Reade also put forward the suggestion that one halogen atom in the tri-halide acts as the kernel atom round which the other halogen atoms and the positive radical are co-ordinated. On London's theory of valency of the halogens to this central kernel atom can be ascribed the valencies 3, 5 or 7 in the tri-, penta-, or hepta-halides. The structures of the polyhalides are therefore



where R stands for the univalent positive radical and X, for either chlorine, bromine or iodine. The double arrows stand for electron-pair bonds and the opposite directions represent opposite spin.

The above mentioned electron configurations of the kernel halogen atom shows that incomplete electron sub-shells are being formed due to polyhalide formation. As is well known, the paramagnetic properties of the rare earths and the transition series elements are due to the presence of incomplete electron sub-shells so the kernel atom in the polyhalides should be expected to show paramagnetism due to the change in the electron configuration on polyhalide formation. This has been experimentally verified by the work of Gray and Dakers (*loc. cit.*). They found that the diamagnetic susceptibilities of the polyhalides calculated from the values of the atomic diamagnetic susceptibilities and the additivity rule, are always in excess of the values obtained experimentally. This is evidently due to the development of feeble paramagnetism. Thus the magnetic susceptibilities of the polyhalides furnish strong evidence for the structure suggested in this paper.

In the case of the polyhalides of the alkali metals of lower atomic weight and metals of alkaline earths, Ray (*loc. cit.*) suggested a structure based on the theory of electrostatic attraction. The properties of the polyhalides of the alkali metals and substituted ammonium radicals are different in more than one respect; the former are soluble in water but sparingly soluble in non-dissociating organic solvents and they are more or less unstable, while the latter are insoluble in water but soluble in non-polar organic solvents and are fairly stable. From this it appears that there is some probablity of a structural difference between these two series of compounds and that polyhalides of the alkali metals and metals of alkaline earths contain polar linkages and with the increase in the volume of the cation, the polar property gradually diminishes until in the case of the substituted ammonium polyhalides the linkage becomes a co-valent one.

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ANALYTICAL USES OF NESSLER'S REAGENT. PART III. ESTIMATION OF FORMALDEHYDE, PYROGALLOL, TANNIC AND GALLIC ACIDS, THEIR ABSOLUTE OXYGEN VALUES.

BY M. GOSWAMI AND A. SHAHA.

In previous papers on the subject (*J. Indian Chem. Soc.*, 1935, **12**, 714 ; 1936, **13**, 73, 315) it has been shown by one of us that alkaline solution of potassium mercuric iodide in presence of reducing sugars gives up iodine, by which they are oxidised, and liberates corresponding amount of mercury according to the degree of reducibilities of the latter, the complex breaking up thus:—

$$2K_2HgI_4 \rightarrow 4KI + Hg_2I_2 + I_2 \rightarrow 2KI + K_2HgI_4 + Hg + I_2$$

This reaction has been previously utilised in estimating formaldehyde in concentrated solution (Gross and Bougoult, *J. Pharm. chim.*, 1922, **26**, 5, 170). It was thought interesting to see whether this method could be utilised in the micro-estimation of CH_2O, and whether the reaction

$$CH_2O + K_2HgI_4 \rightarrow Hg + H{\cdot}COOH$$

is absolute and strictly quantitative. For this purpose definite amount of pure dry hexamethylenetetramine was distilled with dilute sulphuric acid (reagent) at 100° and the distillate was absorbed in alkaline Nessler's solution. The mercury liberated was dissolved in standard iodine solution and the excess of the latter was titrated back. The results obtained were found to conform strictly to the above equation. The micro-estimation also gave excellent results and a dilution of 1 in 100,000 was estimated with fair degree of accuracy. This encouraged us to see the applicability of the method in finding out the absolute oxygen value of pyrogallol and, therefore, in estimating it quantitatively. Previous experimenters have given different results about the capacity of alkaline pyrogallol to absorb oxygen (Berthelot, *Compt. rend.*, 1893, 1066, 1459; Zorkocyz, *Biochem. Z.*, 1925, 161). Thus Berthelot (*loc. cit.*) found that according to the nature and strength of the alkali used, the absorption varied from 1-3 atoms of oxygen per molecule of pyrogallol, whereas according to Zorkocyz it goes beyond to 5 atoms. By the application of potassium mercuric iodide method constant results were obtained and it was found that one molecule of pyrogallol always liberated two atoms of mercury corresponding to two atoms of oxygen. The experiments were done in absence of oxygen. This led us to examine the reducibilities of tannic and gallic acids. Unlike pyrogallol these estimations could be done in open air and it was found that one molecule of tannin (pentadigalloylglucose) absorbed 16 atoms of oxygen, whilst 4 molecules of gallic acid took 11 atoms. Various dilutions have been tested and fairly accurate results have been obtained. The method can, therefore, be suitably applied for their quantitative estimations.

EXPERIMENTAL

Absolute Oxygen Value and Micro-estimation of Formaldehyde.

Hexamethylenetetramine solution (5 c.c.; 250 c.c. containing 0·030201 g.) corresponding to 0·007767 g. of CH_2O, was taken in a flask fitted with a dropping funnel, trap and a condenser; the end of the latter was connected with a funnel and fitted in a wide-mouthed bottle containing alkaline Nessler's solution. This was followed by a second bottle containing the same solution and serving as a guard. The Nessler's solution used in this and other experiments described in the paper was of the following strength:—2·5 g. of $HgCl_2$; 8 g. of KI; 100 c.c. of water; 50 c c. of 30 % NaOH. Pure H_2SO_4 (15 %, 35 c.c.) was added from the funnel to the tetramine solution and the whole was distilled; mercury was precipitated in the first bottle, the second one remaining practically unaffected. The solutions of both were mixed, acidified with glacial acetic acid and standard iodine solution added. After the liberated mercury dissolved, the excess of iodine was titrated back. Several similar distillations were done and the following are some of the results.

TABLE I.

CH_2O actual in 5 c.c. calculated from $(CH_2)_6N_4$.	CH_2O found calc. on the basis that each mol. takes 1 atom of oxygen.
0·007767 g.	0·007668 g.
"	0·007752
"	0·0078349
"	0·007752

Micro-estimation.—Pure formaldehyde solution of definite strength was prepared from $(CH_2)_6N_4$ by distillation with pure sulphuric acid. Micro-estimation was done using $N/100$-thiosulphate and iodine solutions. The following are some of the results.

TABLE II.

Actual CH_2O present.	CH_2O found.
0.0525 %	0·0525 %
0·0217	0·0211
0·0108	0.01056
0·00534	0·00559
0·00107	0·00091

Absolute Oxygen Value of Pyrogallol and its Estimation.

The experiment was done in the apparatus shown in Fig. 1. It was

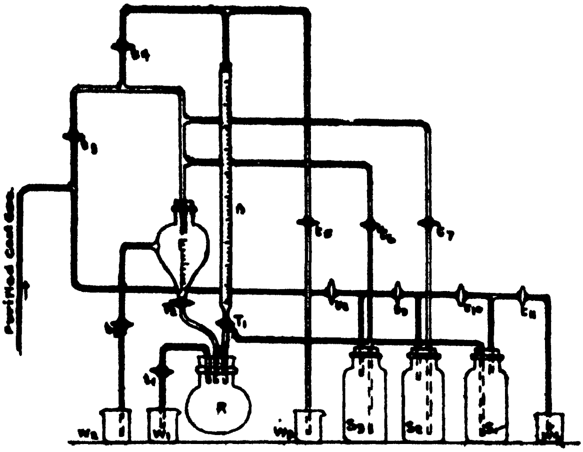

FIG. I.

made air-free by means of coal gas purified and freed from oxygen by passing it successively through alkaline pyrogallol, bromine water, caustic soda and sulphuric acid. Carefully prepared air-free water was used to prepare standard pyrogallol (S_1) and Nessler's solution (S_2). The pushing up of these solutions and glacial acetic acid (S_2) in the burette B(for S_1) and in the graduated funnel F(for S_2 and S_3) as well as the introduction of them in R, the reaction vessel, were all done in the atmosphere of coal gas by opening and closing the respective stop-cocks $t_1 - t_{11}$, T_1 and the two-way cock T_2 (connecting B with R and B with S_1) and by using one or more of the the water seals $w_1 - w_4$ to drive off air or to release the gas pressure inside the system. At first the whole apparatus was made air-free with empty S_1, then closing all other stop-cocks, the latter was detached and standard pyrogallol was quickly introduced in it which was then connected with the system and made air-free by closing and opening the relevant stop-cocks. This precaution was neccssary as it was undesirable to pass all the air of the system through pyrogallol solution.

The apparatus was made air-free in the following way: —

Parts made air-free.	Stop-cocks closed.	Stop-cocks opened.
Tube containing $t_8 - t_{11}$	t_3	$t_8 - t_{11}$
S_1	$t_5 - t_{10}$, T_2, t_2	T_1(connecting B with S_1), t_3, t_4, t_{11},
S_3	T_2, t_2, t_4, t_7, t_8	t_3, t_6, $t_9 - t_{11}$.
S_2	T_2, t_2, t_4, t_6, t_9	t_3, t_7, t_{10}, t_{11}.
F	T_2, t_4, $t_5 - t_8$	t_2, t_3.
F&R	T_1, t_2, t_4, $t_5 - t_8$	T_2, t_1, t_3.
F,R&B	t_1, t_2, t_4, $t_6 - t_8$	T_1 (connecting B with R), T_2, t_2, t_5.
Tube containing t_4&t_5	T_1, T_2, t_2, $t_6 - t_8$	$t_3 - t_5$.

The solutions were pushed up in the following way :—

Solution contained in	Stop-cocks closed.	Stop-cocks opened.
S_1	t_2, t_6, t_7, t_{11}	T_1 (con. B with S_1), t_3, $t_8 - t_{10}$.

(The pressure was released by opening t_{11} and closing T_1 : the liquid B is adjusted to the desired mark by connecting B and S_1 by T_1)

Solutions contained in	Stop-cocks closed.	Stop-cocks opened.
S_2	t_3, t_6, t_{10}, T_2	$t_7 - t_9$, t_2.

(The pressure was released by opening t_{10} and t_{11})

S_3	t_3, t_9, T_2	t_6, t_8, t_2.

(The pressure was released by opening $t_9 - t_{11}$)

The solutions were introduced in R in the following way :—

Solution	Stop-cocks closed.	Stop-cocks opened.
Standard pyrogallol from B	t_2, $t_5 - t_{11}$, T_2	t_3, t_4, t_1, T_1 (connecting B with R).
Nessler's solution and glacial acetic acid from F.	$t_4 - t_{11}$, t_2	t_3, T_2, t_1.

Measured amount of the standard solution was taken in R from the burette and Nessler's solution and glacial acetic acid (10 c.c. each) were added in succession from the graduated funnel. Without disturbing the apparatus R was detached and the mercury liberated was dissolved in standard iodine solution (10 c.c), the excess of the latter was then at once titrated back. The following are the results:—

TABLE III.

Thiosulphate = 0·1042*N*.

Pyrogallol in 250 c.c.	Vol. taken.	Thiosulphate required		Pyrogallol	
		Before oxidation (A).	After oxidation (B).	Found : (A − B) × thio × 0·00315.	Actual.
0·1907 g.	10 c.c	8·8 c.c.	6·5 c.c.	0·007549 g.	0·007628 g.
0·4960	1	,,	8·2	0·001969	0·001984
1·2551	1	,,	7·25	0·005087	0·00502
2·3412	1	,,	5·9	0·009517	0·009361

Pyrogallol found was calculated on the basis that one molecule takes two atoms of oxygen.

Oxygen Value and Estimation of Tannic and Gallic Acids.

Unlike pyrogallol tannic and gallic acids could be treated in open air. The procedure was the same.

Merck's tannic acid (guaranteed reagent, Pentadigalloylglucose, M. W. 1700) was taken. The following are the results :

TABLE IV.

0·05112 *N*-Thiosulphate and 10 c.c. of iodine were used,

Tannic acid in 250 c.c.	Vol. added.	Thiosulphate required		Tannic acid	
		Before oxidation (A).	After oxidation (B).	Found : (A – B) × thio. × 0·0053.	Actual.
0·3020 g.	10 c.c.	15·5 c.c.	11 c.c.	0·01219 g.	0·01208 g.
0·7373	1	,,	14·35	0·003116	0·002949
1·1919	1	,,	13 7	0·004877	0·004768
2·2988	1	,,	12·1	0·009212	0·009195

Tannic acid found was calculated on the basis that 16 atoms of oxygen were required for one molecule.

Merck's pure gallic acid was taken and recrystallised from hot water. The following are the results: (Gallic acid found was calculated on the basis that 4 molecules required 11 atoms of oxygen).

TABLE V.

Gallic acid in 250 c.c.	Vol. added.	Thiosulphate required.		Gallic acid	
		Before oxidation (A).	After oxidation (B).	Found : (A – B) × thio × 0·0053.	Actual.
0·2775 g.	10 c.c.	17·2 c.c.	10·55 c.c.	0·01135	0·01110
0·3614		,,	8·55	0·01452	0·01446
1·2019	1	,,	14·3	0·004938	0·004808

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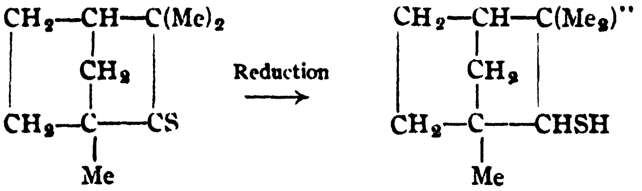
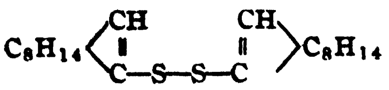
STUDIES IN THE CAMPHOR SERIES. PART IV. SYNTHESIS OF THIOFENCHONE AND TWO ISOMERIC BIS-THIOCAMPHORS AND THEIR DERIVATIVES.

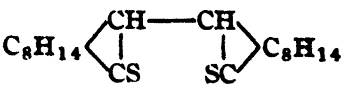
By Dines Chandra Sen.

Thiofenchone, previously prepared by Rimini (*Gazzetta*, 1909, **39**, 203), has been obtained as a deep red liquid by the simultaneous action of dry hydrogen chloride and sulphuretted hydrogen at 0° on freshly distilled fenchone in alcoholic solution. Like a ketone it gives with evolution of sulphuretted hydrogen a semicarbazone and an oxime which are found to be identical with those of fenchone. On reduction with aluminium amalgam, it gives thiofenchol. It forms also a white crystalline mercury salt with mercuric acetate. It decolourises iodine and permanganate solutions and also forms a yellow silver salt. All these properties lead to the following constitutional formulæ of thiofenchone and thiofenchol:



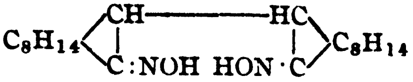
The reactive nature of the methylene group due to the negative influence of a thiocarbonyl group (*cf.* Sen, *J. Indian Chem. Soc.*, 1935, **12**, 751; 1936, **13**, 523; *Nature*, 1936, **138**, 548) has made it possible to synthesise two isomeric bis-thiocamphors by the action of iodine on the sodio derivative of thiocamphor in boiling benzene. Bis-thiocamphor can be represented by either (I) or (II).


(I)

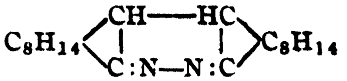

(II)

Oddo's method (*cf.* *Gazzetta*, 1897, **27**, 149; 1911, **41**, 126; *Ber.*, 1904, **37**, 1569) of synthesis of bis-camphor, namely by the action of sodium or magnesium on α-bromocamphor cannot be applied for the synthesis of bis-thiocamphor, as α-bromothiocamphor cannot be prepared in the pure state. The action of iodine on sodio-camphor in benzene on the other hand gives α-iodocamphor instead of bis-camphor.

dl-Bis-thiocamphor (m.p. 164°) forms a dioxime, (m.p. 199°, decomp.) and an azine (m.p. 176°), and *l*-bis-thiocamphor (m.p. 180°) also forms an azine (m.p. 200°) under similar conditions. These facts, along with the analytical and molecular weight data of the two bis-thiocamphors and their derivatives lead to the conclusion that they contain two C:S groups, and that they are 1:4-dithioketones, and have the formula (II). The dioximes and the azines should, therefore, be represented by the structures (III) and (IV) respectively.



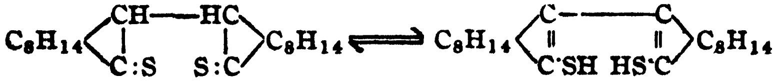
(III)



(IV).

On reduction with aluminium amalgam in moist ethereal solution, *dl*-bis-thiocamphor forms *dl*-bis-thioborneol, m.p. 148°, which decolourises iodine and forms a yellow lead salt.

l-Bis-thiocamphor has a very high molecular rotation, $[M]^{30}_{D}$ = −1109·5 in benzene solution, whereas the molecular rotation of *l*-thiocamphor is $[M]^{30}_{D}$ = −41·3 in the same solvent and under similar conditions. This high exaltation in optical activity may be attributed to the presence of a potential conjugated system in bis-thiocamphor, which may behave both in the thio and thiol phases.



Studies in absorption spectra in the visible region of bis-thiocamphor at different dilutions and the comparison of these with those of thiofenchone and thiocamphor have given interesting results. It has been noticed that a 5·4% solution of bis-thiocamphor in benzene manifests a characteristic absorption band between 5270Å and 4530Å and that with dilution this band becomes shorter corresponding to dilutions 4·5% and 3·6%. Finally at 2·7% concentration it gives a very short band having the centre at 4950Å. Similar bands have also been observed in the case of *l*-thiocamphor and *d*-thiofenchone. This selective absorption band is, therefore, a characteristic property of the chromophoric C:S group in cyclic thioketones.

EXPERIMENTAL.

Thiofenchone.—A simultaneous current of hydrogen chloride and sulphuretted hydrogen was passed for 6 hours into an alcoholic solution of freshly distilled fenchone (50 g.). The product was poured into water and extracted with ether. The ethereal solution was dried over sodium sulphate, ether removed and the residual liquid distilled in vacuum. On repeated fractionation, thiofenchone distilled at 92°/5 mm. (215-16°/762 mm.) as a red liquid having camphoric smell, yield 5 g. [Found: C, 71·21; H, 9·63; S, 19·12; M.W. (cryoscopic in benzene), 167. Calc. for $C_{10}H_{16}S$: C, 71·43; H, 9·52; S, 19·05 per cent. M.W., 168]. The *oxime* was prepared by the action of hydroxylamine hydrochloride in pyridine solution, m.p. 159°. (Found: N, 8·35. Calc. for $C_{10}H_{17}ON$: N, 8·38 per cent). The *semicarbazone* was prepared by the action of semicarbazide hydrochloride on thiofenchone in alcoholic solution, m.p. 172°. (Found: N, 20·15. Calc. for $C_{11}H_{19}ON_3$: N, 20·09 per cent). These derivatives have been found to be identical with fenchone oxime and fenchone semicarbazone.

Reduction of Thiofenchone.—Thiofenchone was reduced by aluminium amalgam in a similar manner as described in the case of thiocamphor (*cf.* Sen, *J. Indian Chem. Soc.*, 1935, **12**, 647) in moist ethereal solution. The ethereal solution was evaporated and the residue treated with a concentrated solution of lead acetate (lead salt of thiofenchol being fairly soluble in alcohol, the solution of lead salt should be very concentrated). The precipitated lead salt was filtered off, suspended in alcohol and decomposed by means of sulphuretted hydrogen. The oil was precipitated from the alcoholic solution and extracted with ether, dried over sodium sulphate, ether evaporated and the liquid distilled at 95°/5 mm. or at 216°-220°/762 mm. It was obtained as a *colourless* liquid having a smell similar to that of thioborneol. (Found: C, 70·68; H, 10·75; S, 18·91. Calc. for $C_{10}H_{18}S$: C, 70·59; H, 10·59; S, 18·82 per cent). Thiofenchol decolourises bromine and iodine solutions and also dilute potassium permanganate solution in the cold.

l-*Bis-thiocamphor.*—A solution of dry *l*-thiocamphor (20 g.) in sodium-dried benzene (50 c. c.) was treated with powdered sodamide (4·8 g.) and the solution boiled for nearly 1 hour under reflux, till the red colour of thiocamphor completely vanished. A solution of iodine (15 g.) in benzene was then added drop by drop to the boiling solution. The boiling was continued for half an hour more and the solution treated with ice-cold water. The benzene solution was washed with water and sodium thiosulphate solution, dried over sodium sulphate and the benzene distilled. The viscous liquid solidified on stirring and it was washed with alcohol which removed the tarry matter. The residual solid on crystallisation from alcohol gave orange hexagonal plates, m p. 180°, yield 6 g.

It is moderately soluble in alcohol and readily soluble in benzene giving a deep red solution. It has the normal molecular weight and is *laevo*-rotatory, $[\alpha]^{30}_{D} = -332{\cdot}1$ in 1 per cent. solution in benzene observed in a 2 dcm. tube. [Found . C, 71·81 ; H, 9·12 ; S, 19·26. M. W. (in benzene, cryoscopic), 332. $C_{20}H_{30}S_2$ requires C, 71·86 ; H, 8·98 ; S, 19·16 per cent. M. W., 336].

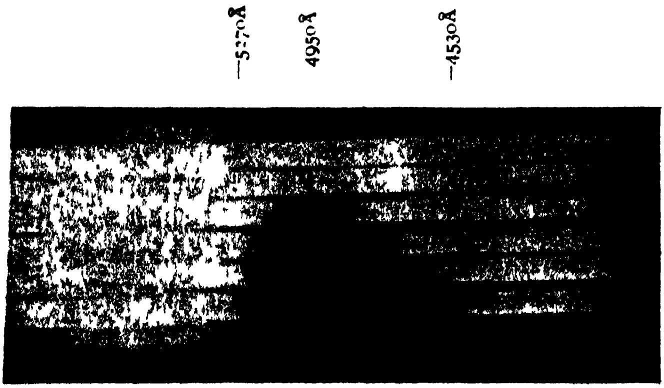
The *dioxime* was prepared by heating *l*-bis-thiocamphor (1 g.) in pyridine (5 c. c.) with hydroxylamine hydrochloride (1 g.). The solution was heated at 100° for 1 hour till the evolution of sulphuretted hydrogen was complete and the solution became colourless. It was then poured into water (500 c. c.) and the white precipitate crystallised from alcohol as needles, m.p. 197°, yield 0·6 g. (Found : C, 71·95 ; H, 9·84 ; N, 8·38 per cent. $C_{20}H_{32}O_2N_2$ requires C, 72·2 ; H, 9·64 ; N, 8·43 per cent).

Dicamphane Azine.—A solution of *l*-bis-thiocamphor (2 g.) in alcohol (4 c. c.) was treated with hydrazine hydrate (3 c. c.) in the cold. The formation of azine was accompanied with evolution of sulphuretted hydrogen and the disappearance of the red colour. The solution was poured into water and the precipitate crystallised from alcohol as shining needles, m.p. 200° (decomp.), yield 1·5 g. (Found : C, 79·75 ; H, 9·89 ; N, 9·34. $C_{20}H_{30}N_2$ requires C, 79·47 ; H, 9·93 ; N, 9·27 per cent). It is soluble in all organic solvents and mineral acids. The *picrate* was obtained as yellow shining needles, m. p. 200° (decomp.). (Found : N, 13·35. $C_{26}H_{33}O_7N_5$ requires N, 13·28 per cent).

dl-*Bis-thiocamphor*.—It was prepared in the same manner as *l*-bis-thiocamphor, m. p. 164°. (Found : C, 71·85 ; H, 9·21 ; S, 19·22. M. W, 332. $C_{20}H_{30}S_2$ requires C, 71·86 ; H, 8·98 ; S, 19·16 per cent. M. W, 336). The *dioxime* crystallises from alcohol as needles, m. p. 199° (decomp.). (Found : C, 72·25 ; H, 9·65 ; N, 8·45. $C_{20}H_{32}O_2N_2$ requires C, 72·2 ; H, 9·64 ; N, 8·43 per cent). The corresponding *diazine*, prepared by the action of hydrazine hydrate on the alcoholic solution of *dl*-bis-thiocamphor melts at 176°. (Found : C, 79·53 ; H, 10·03; N, 9·35. $C_{20}H_{30}N_2$ requires C, 79·47 ; H, 9·93 ; N, 9·27 per cent).

Reduction of dl-*bis-thocamphor*: *Preparation of* dl-*bis-thioborneol.*—Aluminium amalgam was added in the cold to the moist ethereal solution of *dl*-bis-thiocamphor (10 g.). The solution was kept for 2 days when reduction was complete, as was evident from the disappearance of the red colour. The solution was filtered off and concentrated after drying over sodium sulphate. It crystallised from alcohol as colourless needles having a characteristic smell like that of thioborneol, m. p. 143°, yield 7 g. (Found: C, 71·25; H, 10·19, S, 19·02. M. W. 338. $C_{20}H_{34}S_2$ requires C, 71·0; H, 10·06; S, 18·04 per cent. M. W, 338).

Determination of Absorption Spectra in the Visible Regions.



The absorption spectra of *l*-thiocamphor, *l*-bis-thiocamphor and thiofenchone in benzene were determined in quartz cell of thickness 0·5 cm. and the variations of the bands with dilutions are shown in the accompanying plate. Spectra corresponding to the following dilutions were compared, (1) 5·4%, (2) 4·5%, (3) 3·6%, (4) 2·7%, and it was noticed that at 5·4% concentration all the substances gave an absorption band beeween 5270Å –4530Å having the band centre at 4950Å, corresponding to dilution of 2·7 per cent.

My thanks are due to Sir P. C. Rây for his kind encouragement during the investigation and also for the facilities in his laboratory.

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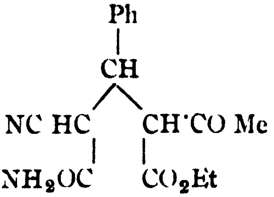
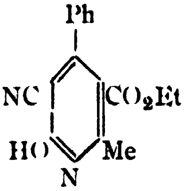
A MODIFICATION OF THE GUARESCHI PYRIDINE SYNTHESIS. PART I.

By Nirmalananda Palit.

A method for the Guareschi pyridine synthesis originated in the observation that when a mixture of cyanoacetic ester and ethylideneacetoacetic ester was treated with ammonia, a dicyano-imide was obtained together with a little dihydrocollidine dicarboxylic ester and a third substance of unknown constitution (*Chem. Zentrl.*, 1897, I, 927 ; Quenda, *ibid.*, 903). The formation of these compounds is explained by a preceding hydrolysis of the ethylidene derivative. With benzaldehyde, the esters and ammonia, Guareschi obtained a compound melting at 222-23°. Later on (*ibid.*, 1907, I, 332) he observed that the product in this case also was a complex mixture, one component of which, (m.p. 225-26°) was definitely characterised to be the open-chain amide (I), while a second, (m.p. 226-27°) was claimed to be oxypyridine (II), derived from (I) by loss of water and hydrogen.



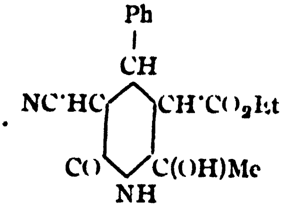
(I)



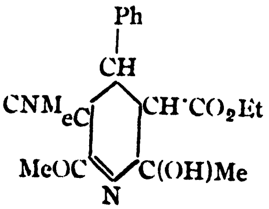
(II)

The compound (m.p. 222-23°) is not mentioned in this later work. It will be noticed that all the above three compounds have very close melting points and it appears necessary to reinvestigate the matter to determine their constitution and to see if they are all really different. At the outset, it was thought advisable to reduce the complex nature of Guareschi's reaction by coupling the four reactants in pairs and to treat the resulting benzylideneacetoacetic ester and cyanoacetamide with a more suitable condensing agent. Thus with a few drops of diethylamine, the condensation proceeded very smoothly and deposited crystals, m. p. 222-23°, in 68%, yield. No other compound could be obtained by varying the conditions. Guareschi's experiment in itself was then repeated in aqueous solution and it was found that only two products could be isolated, one, the same as before, m.p. 222-23°, and the other, the open-chain amide (I), m.p. 225-26°, the former or the latter preponderating according as the temperature was maintained low with ice or not. It is doubtful if the pyridone (II) is formed at all. The amide having been definitely characterised, the former compound was taken up for elucidation of its constitution. Analysis showed it to be an addition product ($C_{16}H_{18}O_4N_2$) but its properties could not be reconciled to the open-chan structure (I), for it did not evolve any ammonia with boiling caustic soda but dissolved to give a yellow solution to be reprecipitated by acids, redissolving in slight excess of the latter and reappearing on allowing the solution to stand. There is no doubt that the primary reaction is an addition between the two molecules, for on boiling with dilute hydrochloric acid for three hours the substance dissolved and the solution after evaporation and extraction with ether, gives an acid, m.p. 82°. This was identified to be β-phenyl-γ-acetylbutyric acid (Knoevenagel and Fries, *Ber.*, 1898, **31**, 762).

In the literature a parallel case has been recorded (Barat, *J. Indian Chem. Soc.*, 1930, **7**, 322). Allen and Scarrow (*Canadian J. Res.*, 1934, **11**, 395) condensed cyanoacetamide with unsaturated ketones and obtained additive products with similar properties. To such compounds they have attributed a cyclic aldol structure due to tautomerisation between the amido and carbonyl groups in 1 : 6 position. The compound in question is also probably best represented by a ring structure, for in addition to the anomalous properties of its amido group, the absence of any carbonyl in it was established beyond doubt. It did not form any semicarbazone, was oxidised to a gum with sodium hypobromite solution and to benzoic acid with chromic acid. It failed to react with Grignard reagent in ether suspension or boiling pyridine solution. It, therefore, may be represented as (III) but it differs in many of its reactions from the similar ring



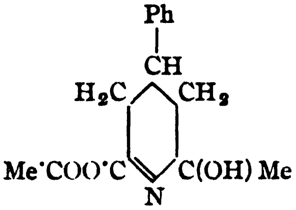
(III)



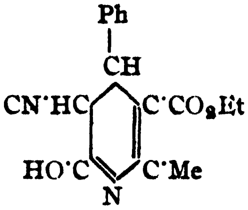
(IV)

compounds of Barat (*loc. cit.*) and of Allen and Scarrow (*loc. cit.*). Thus with dimethyl sulphate two methyl groups are introduced but the product is a monomethoxy derivative and is presumably represented by (IV). The aldol structure, on dehydration, was excepted to pass readily into Guareschi's compound (II). In acetic anhydride suspension, addition of a few drops of strong sulphuric acid caused it to warm up and go rapidly into solution, but it was attended with considerable decomposition of material with evolution of carbon dioxide even though it was cooled in ice. Replacement of the acid by the pyridine gave better result when heated under reflux for two hours and the product on analysis was found to agree with the formula $C_{14}H_{17}O_3N$ (V) derived from the parent substance by withdrawal of the cyano and carbethoxy groups, followed by acetylation (*cf.* Allen and Scarrow, *loc. cit.*). This structure explains its insolubility in caustic soda. Alcoholic sulphuric acid, hot caustic soda or even barium hydroxide ruptures the ring.

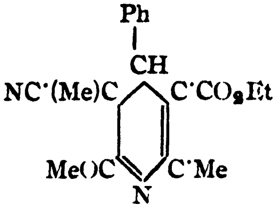
It is indeed very surprising to note that all attempts to dehydrate (III) with phosphorus pentachloride, pentoxide or hydrogen chloride in dry chloroform solution met with failure until with a controlled action of phosphorus trichloride in boiling benzene, the compound (VI) was obtained.



(V)



(VI)

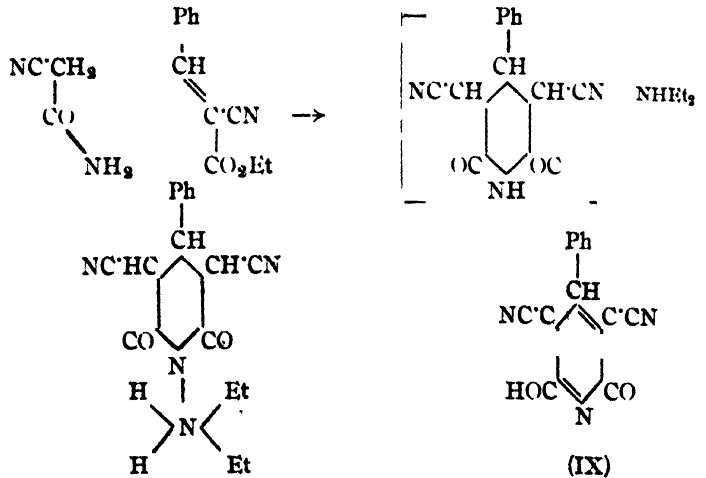


(VII)

Like the parent substance, it dissolves in alkali with a yellow colour. It melts at 142° and is different from Guareschi's pyridone (II). That during dehydration, hydrogen atoms are not eliminated is indicated by its ready transformation into (VII) with dimethyl sulphate.

The ring formation by tautomerisation of amide hydrogen atom seemed very interesting and such abnormal reactivity may be attributed to the fact that in (I), the amide group acquires certain mobility due to its position next to carbonyl and the very close proximity of a second carbonyl of the acetoacetic ester residue, being in the sixth position with regard to it. It would thus appear that the non-existence of one of these negative groups would render it incapable of forming the ring. To test this view cyanoacetamide was conveniently replaced by the dinitriles of Mayer (aminoarylacrylonitriles) which are capable of reacting in the tautemeric from $\mathrm{R\,C\,(:N\,H)\cdot CH_2CN}$. These appeared to be far less reactive towards the unsaturated ester and if condensation could be effected, the products were not analogous in all cases. Before a definite conclusion may be drawn, the results require a more critical examination and will be communicated shortly.

In the above condensations benzylidene-acetoacetic ester was next replaced by benzylidene-cyanoacetic ester. Cyanoacetamide readilly combined in presence of diethylamine and needle shaped crystals (m. p. 266-68°) began to separate within an hour. On allowing the mixture to stand at room temperature for several days, it was noticed that the needles were entirely replaced by small grains, m. p. 245°. Both the substances in amyl alcohol give a deep brown colouration with ferric chloride. The latter is a dicyano-oxypyridone (IX), already obtained by Guareschi (*Chem. Zentrl.* 1899, II, 118) and by Day and Thorpe (*J. Chem. Soc.*, 1920, **117**, 1473) by different methods. Its sodio derivative is the only product when sodium ethoxide is employed as the condensing agent. The former compound passes into the latter quickly on boiling with acids. The analytical data agree with the formula $C_{17}H_{20}O_2N_4$ and it evolves with alkali a gas having an ammoniacal smell but not tarnishing Nessler's solution. Since the diones are known to possess marked acidic properties it appears to be a diethylammonium salt (VIII) produced according to the following scheme.



(VIII)

(IX)

EXPERIMENTAL.

Condensation of Cyonoacetamide with Benzylidene-acetoactic Ester: Formation of 5-Cyano-6-keto-2-oxy-2-methyl-3-carbethoxy-4-phenylpiperidine.—Cyanoacetamide (0·8 g) and benzylidene acetoacetic ester (2·2 g.) (Knoevenagel, *Ber.*, 1896, **17**, 2) were dissolved in sufficient warm alcohol so that the amide did not crystallise out on cooling. A few drops of diethylamine were added when the solution warmed up considerably and the colour gradually darkened to dirty brown. After keeping overnight the crystals separating were collected and washed with alcohol. Colourless needles from alcohol m. p. 222-23°, yield 1·7 g. It is soluble in acetone and in hot caustic soda with a yellow colour. (Found : C, 63·54 ; H, 6·24 ; N, 9·53. $C_{16}H_{18}O_4N_2$ requires C, 63·57 ; H, 5·96 ; N, 9·27 per cent).

Hydrolysis : Formation of β-Phenyl-γ-acetylbutyric Acid.—A suspension of the substance in dilute hydrochloric acid was boiled under reflux and in 2 hours a perfect solution was obtained. On cooling it became milky and after another 2 hours a small quantity of oil separated. On allowing to stand overnight, preferably in an ice-chest, clusters of needles were obtained. The mother liquor on evaporation and extraction with ether gives a second crop. The total quantity was crystallised from water, m. p. 82°. (Found : C, 69·70 ; H, 6·99. $C_{12}H_{14}O_3$ requires C, 69·90 ; H, 6·79 per cent).

Methylation : Formation of 5-Cyano-6-methoxy-2-oxy-2 : 5-dimethyl-3-carbethoxy-4-phenyltetrahydropyridine.—On adding dimethyl sulphate to the warm solution of the substance in caustic soda (10%) a gummy mass separated. On allowing it to stand in water for 2 days it solidified. It was twice crystallised from alcohol, m. p. 162°. (Found : C, 65·23 ; H, 6·52 ; OMe, 9·61. $C_{18}H_{22}O_4N_2$ requires C, 65·45 ; H, 6·66 ; OMe, 9·4 per cent).

Reaction with Acetic Anhydride.—The substance was suspended in acetic anhydride with a drop of pyridine and boiled. Prolonged heating darkened the colour and on pouring into water and allowing to stand, it separated in the form of needles. It crystallised from dilute alcohol, m.p. 145-46°. (Found : C, 68·25 ; H, 6·82 ; N, 6·11. $C_{14}H_{17}O_3N$ requires C, 68·01 ; H, 6·88 ; N, 5·74 per cent).

Treatment with Phosphorus Trichlorde : Formation of 5-Cyano-6-oxy-3-carbethoxy-2-methyl-4-phenyl-4 5-dyhydropyridine.—The substance in benzene suspension was heated for about 2 hours on a water-bath with phosphorus trichloride. A gummy mass was obtained from which the product could be isolated with difficulty in extremely poor yield. The operation was much more successful when the mixture after boiling was evaporated, treated with water, extracted with ether, the extract repeatedly washed and evaporated. The residue was a pale yellow solid which crystallised from water containing acetic acid, m. p. 142°. (Found: C, 67·81 ; H, 5·88 ; N, 10·10. $C_{16}H_{16}O_3N_2$ requires C, 67·60 ; H, 5·6 ; N, 9·86 per cent).

The Methylation of the above compound with dimethyl sulphate produced an oil which solidified after 2 days. It crystallised from methyl alcohol, m. p. 149°. (Found : C, 69·52 ; H, 6·44 ; N, 9·25 ; OMe, 10·11. $C_{18}H_{20}O_3N_2$ requires C, 69·23 ; H, 6·41 ; N, 8·97 ; OMe, 9·93 per cent).

Condensation of Cyanoacetamide with Benzylidene-cyanoacetic Ester: (i) *Formation of Diethyl ammonium salt of 3:5-Dicyano-2:6-diketo-4-phenyl-piperidine.*—The solution of the amide (0·8 g) and the ester (2 g.) in absolute alcohol was treated with diethylamine. After keeping overnight at room temperature it set to a mass of white needles. It is almost insoluble in alcohol, acetone, benzene, etc. It crystallises from amyl alcohol or pyridine in flat lancet like needles, m. p. 268° ; yield 1·4 g. It dissolves in warm water and on adding concentrated hydrochloric acid to the cooled solution a white mass is obtained, m. p. 245° (see belew). (Found : C, 65·12 ; H, 6·2 ; N, 17·8. $C_{17}H_{20}O_2N_4$ requires C, 65·38 ; H, 6·4 ; N, 17·94 per cent).

(ii) *Formation of 3 : 5-Dicyano-6-hydroxy-4-phenyl-$\Delta^{3:6}$-dihydro-2-pyridone.*—If in the above condensation, the mixture was allowed to stand for 4-5 days, the needles separating were gradually entirely replaced by pale greenish cubes, m. p. 245°. It dissolves in boiling water and the aqueous solution on acidification precipitates the substance as a white shining mass. (Found : C, 65·58 ; H, 3·40 ; N, 17·92. $C_{13}H_7O_2N_3$ requires C, 65·8 ; H, 2·9 ; N, 17·7 per cent).

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ON THE PHYSICO-CHEMICAL PROPERTIES OF ELECTRO-DIALYSED GELS OF SILICA, ALUMINA, FERRIC HYDROXIDE AND THEIR MIXTURES. PART III. CATAPHORETIC VELOCITY AND P_H.

BY PROMODE BEHARI BHATTACHARYYA.

In two previous papers of this series the ion exchange properties (*J. Indian Chem. Soc.*, 1936, **13**, 204) and moisture retention capacity (*ibid.*, 1936, **13**, 547) of the above synthetic gels have been described. A comparative study has also been made of these properties of gels, which are probable constituents of soils, with the properties of soil colloids. In the present investigation the cataphoretic velocity and p_H of the gels, saturated with different cations, have been studied.

The effect of substitution of cation on migration velocity of soil colloids has been studied by various investigators notably by Mattson (*First Int. Cong. Soil Sci.*, 1928, **2**, 185, 199; *Soil Sci.*, 1929, **28**, 373), Anderson (*J. Agric. Res.*, 1929, **38**, 565) and Bradfield (*J. Phys. Chem.*, 1931, **35**, 369). An attempt has been made to make a comparative study of the results obtained by these investigators and those obtained by the author. In this connection reference may also be made to the works of Abramson (*J. Phys. Chem.*, 1931, **35**, 289), Mooney (*ibid.*, 1931, **35**, 331) and Kemp (*Trans. Faraday Soc.*, 1935, **31**, 1347).

The cataphoretic velocity of the particles was determined by the microscopic method in a rectangular cataphoretic cell as designed by Freundlich and Abramson (*Z. physikal. Chem.*, 1927, **128**, 25). Velocities were measured at different depths of the cell and they were found to lie on a parabolic curve, in good agreement with Smoluchowski's equation,

$$V_P = \underset{\text{(I)}}{\frac{3}{4} V_{\frac{1}{6}} + \frac{1}{4} V_{\frac{1}{2}}} = \underset{\text{(II)}}{V_{\frac{1}{5}}} = \underset{\text{(III)}}{V_{\frac{4}{5}}}$$

The velocity was also calculated from the equation,

$$\underset{\text{(IV)}}{V_P = \frac{1}{x_1}\int_0^{x_1} vdx,}$$

where the value of vdx was obtained from graphical representation.

Velocities obtained as in (I), (II), (III) & (IV) were found to agree quite well and the mean of all these velocities was taken as the true particle velocity.

EXPERIMENTAL.

A potential of 200 volts from a set of storage batteries was applied to the cataphoretic cell. The drop in potential in the rectangular part of the cell, which was 5·75 cm. long, was calculated from a determination of the relative resistances of the liquid in the rectangular flat part of the cell and in the attached limbs.

The method of preparing the gels and saturating them with various cations have been described in Part I of this series of papers (*loc. cit.*).

The particles of the saturated gels, which were washed until the concentration of Cl′ ion in the filtrate was less than 1×10^{-5} (*loc. cit.*) were suspended in water, shaken, and allowed to settle to remove coarser particles by sedimentation. Time required for settling was calculated from Stokes' formula so that particles above diameter of 0·01 mm. could be removed by sedimentation, assuming them to be spherical. The cell was dismantled after each determination and cleansed thoroughly so that no appreciable error could be introduced by particles sticking to the walls of the cell.

The p_H values of the suspensions were determined by means of hydrogen and quinhydrone electrodes. The proportion of gel to water was 1 : 2·5 in all cases Results are given in the following tables.

TABLE I.

Sample.	Saturating cation.	Cataphoretic velocity. μ/sec. volt/cm.	Temp.	p_H.
SiO_2	...	−0·58	29·0	4·91
	Na	−1·11	29·5	5·20
	K	−0·78	29·0	5·59
	Ca	−0·56	30·0	5·22
	Mg	−0·76	29·0	5·54
Al_2O_3	...	+0·83	29·5	5·87
	Na	+0·30	30·0	6·86
	K	+0·44	30·0	6·79
	Ca	+0·80	29·5	6·91
	Mg	+0·59	29·5	6·79
Fe_2O_3	...	+0·48	29·5	5·88
	Na	+0·27	29·0	6·51
	K	+0·34	29·0	6·22
	Ca	+0·46	29·5	6·34
	Mg	+0·39	29·0	6·23

TABLE II.

Sample.	Saturating cation.	Cataphoretic velocity. μ/sec. volt./cm.	Temp.	pH.
$SiO_2 + Al_2O_3$ (Mixture I). $\frac{SiO_2}{Al_2O_3} = 4·37$	...			5·04
	Na			6·42
	K			6·31
	Ca			6·23
	Mg			6·11
$SiO_2 + Al_2O_3$ (Mixture II) $\frac{SiO_2}{Al_2O_3} = 1·33$	...	−0·52	30·5	5·13
	Na	−0·99	30·0	6·41
	K	−0·93	30·0	6·39
	Ca	−0·58	30·0	6·66
	Mg	−0·77	29·5	6·42
$SiO_2 + Fe_2O_3$ (Mixture III) $\frac{SiO_2}{Fe_2O_3} = 3·68$	...			5·37
	Na			6·06
	K			5·91
	Ca			6·22
	Mg			6·10
$SiO_2 + Fe_2O_3$ (Mixture IV) $\frac{SiO_2}{Fe_2O_3} = 1·04$	...	−0·44	29·0	5·78
	Na	−0·85	29·0	6·10
	K	−0·68	30·0	5·87
	Ca	−0·49	29·5	6·37
	Mg	−0·64	29·0	6·31

TABLE III.

Saturating cation.	Anderson clay.	Mattson clay.	Author		
			SiO_2.	$SiO_2 + Al_2O_3$.	$SiO_2 + Fe_2O_3$.
Ca	100	100	100	100	100
Mg	99	...	135	132	130
K	134	...	140	160	140
Na	149	191	198	170	173
H	23	168	104	89	90

DISCUSSION.

The amount of free electrolyte occuring normally in laterite soil of this country of heavy rainfall is very small. In the present investigation, the gels, which are probable constituents of soil, may be assumed to correspond approximately to natural condition. The cataphoretic velocity was determined in suspensions of the samples in distilled water. During recent years this problem has been attacked from all sides. That the particle velocity is independent of size and shape has been shown by various investigators. A list of number of investigators together with the names of the materials with which the investigation was made has been given by Abramson (*J. Phys. Chem.*, 1931, **35**, 289). Mention may be made of the work of Abramson (*J. Amer. Chem. Soc.*, 1928, **50**, 390) and Freundlich and Abramson (*loc. cit.*; *ibid.*, 1928, **133**, 51) who have shown that the velocity of particles of quartz, glass and clay is independent of size and shape between 3μ to 15μ. Recent investigation of Kemp (*loc. cit.*) on the cataphoretic mobility of silica and gamboge has shown that the mobility decreases with decreasing particle size. He accounts for this variation of mobility with particle size by Henry's equation (*Proc. Roy Soc.*, 1931, **A133**, 106)

$$V = \frac{X\sigma}{\eta K} \cdot \frac{Kb}{1 + Kb} \quad f(Kb)$$

over a range of Kb, 2-330, where b is the radius and K is defined by the equation

$$K = \sqrt{\frac{4\pi e^2}{DkT} \Sigma n_1 \gamma_1^2} = 3 \cdot 28. \quad 10^{7}\sqrt{u} \quad \text{at } 20^\circ.$$

According to Henry, however, no variation in the mobility could be expected with large particles in relatively strong solutions. Recently Mukherjee and co-workers (*J. Indian Chem. Soc.*, 1936, **13**, 372, 428) in an investigation on the cataphoretic velocity of colloidal particles, have made a critical study of the dependence of velocity on size, shape and ionic strength. They have shown that the velocity increases with the aggregation of colloidal particles in presence of an electrolyte and this behaviour has been explained from a consideration of Mukherjee's theory of ion adsorption. As stated previously, the presence of free electrolytes in the gels used in this investigation was very small and the velocities were measured in distilled water. The particle size was 0·01 mm. and below. All the experiments were also conducted under identical conditions. Hence no appreciable error may be expected to be introduced in getting comparable results.

Kemp (*loc. cit.*) has shown that the mobilities of the particles of gamboge and silica show very little change with the p_H of the solution. The change in velocity with p_H of materials such as ferric oxide in the sol state has been studied by Hanzel and Ayres (*J. Phys. Chem.*, 1931, **35,** 2930) and others. It will be seen from the tables that the p_H values of the gels used in the experiments all lie between 5 and 7. So the effect of difference of p_H on the velocity, if any, might be neglected and hence a study on the change of velocity with p_H of the particles was not made a part of the investigation.

In Tables I and II are given the p_H and cataphoretic velocity of the unmixed and mixed gels when saturated with different cations. In the case of the SiO_2 gel, Na increased the negative charge to a considerable extent, the cataphoretic speed being in the order Na > K > Mg > Ca > electrodialysed gel (which is an unsaturated hydrogen gel). The values of K- and Mg-saturated samples are very near to each other, where as the Ca-saturated sample gives a value which approaches that of the electrodialysed materials. It will be observed from Table II that the mixed gels of $SiO_2 + Al_2O_3$ and $SiO_2 + Fe_2O_3$, as obtained by mutual precipitation, also behave in the same way as the SiO_2 gel, the speed being in the order Na>K >Mg >Ca > unsaturated H-gel. This order holds for the degree of dispersion of various soil colloidal materials shown by Gedroiz, (*Z. Opytn. Agron.*, 1924, **22,** 29).

In Table III are given the relative values of the mobility of clay particles as obtained by Mattson, Anderson and the author. From a comparison of the results it may be said that the data are in partial agreement with the observations of the investigators named above. Where as Anderson got the lowest value for H-clay, and Mattson obtained a value greater than that of Ca-clay, the values obtained in the present investigation for the unsaturated H-gel are nearer to the value of Ca-gel; but the values are slightly less in the case of the mixed gels and greater in case of SiO_2. According to Keen ("The Physical Properties of the Soil," p. 190) however, the value of Anderson for H-clay is probably incorrect.

The gels of Al_2O_3 and Fe_2O_3, saturated with different cations are electropositive between the p_H range indicated (Table II). The order of effect of ions is again reversed in this case, being electrodyalised gel >Ca > Mg >K >Na. Thus the effect of ions is quite marked in the value of mobility of the gel particles.

p_H values of the gels, saturated with different cations, are given in Tables I and II. The p_H values of pure SiO_2, both gel and powder and of the supernatant liquid, have been given in Part I. An observation of the values of SiO_2 gel might suggest that the gel after saturation with the chlorides and continued washing till fee from chlorine, may adsorb H-ions from water on partial displacement of the metal ion with which the gel has been saturated.

It will be noticed that in all cases except in the case of SiO_2 gel, Na-saturated gel gives higher values than the K-saturated gel; and Ca-saturated gel gives higher value than the Mg-saturated gel. As expected, monovalent cations influence the p_H in the order of their hydration. But in case of bivalent cations this order of hydration does not hold. This may be ascribed to the special characteristics of Ca-saturated colloid observed by Gallay (*Koll. Chem. Beih.*, 1925, **21**, 464) who pointed out that Ca- soils, both artificial and natural, differ from all soils through their greater sensitivity to electrolytes. This view has also been confirmed by Aarnio (*First Int. Cong. Soil Sci.*, 1928, **2**, 65) who observed that the reaction of calcium clay in water solution was always higher than that of Mg- clay.

It has been noted by various investigators that if a soil is adsorptively saturated with the ions of Ca, Mg, Na, and K and if there is no free hydrolysed salt in a soil, then the soil is either neutral or basic. But percolation brings exchange of the cations with hydrogen ions of water and makes the soil at the same time more acid. It will be seen from the tables that the p_H values of the gels never exceeded 7 and in case of SiO_2-gel it became as low as 5·2. This low p_H is evidently due to the continued leaching during washing of the gels after saturation when probably there was a partial exchange of the metal ions with hydrogen ion.

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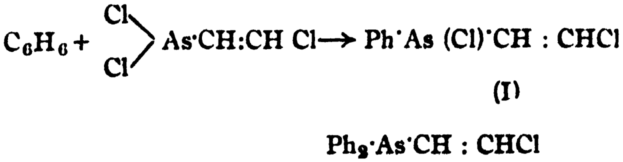
STUDIES IN ORGANO-ARSENIC COMPOUNDS. PART IV. HETEROCYCLIC RING CONTAINING ARSENIC.

By Hirendra Nath Das-Gupta.

Only a few heterocyclic compounds containing arsenic in the ring are known. It appears from literature that no attempt has hitherto been made to synthesise the arsenic analogue of indole. The synthesis of a compound of this type was thought to be interesting not only from theoretical point of view but also from the expected therapeutic activity.*

1-Chloroarsindole has now been synthesised in various ways but the present communication deals with its preparation directly from benzene and β-chlorovinyldichloroarsine (Green and Price, *J. Chem. Soc.*, 1921, **119**, 448). Two distinct types of compounds, *viz.*, (*i*) β-chlorovinylphenylchloroarsine and, (*ii*) β-chlorovinyldiphenylarsine are formed along with a large quantity of liquid and solid by-products by the condensation of benzene and β-chlorovinyldichloroarsine either alone at a high temperature or in the presence of anhydrous aluminium chloride at room temperature. The by-products obtained are of diverse types, but only two could be isolated namely, (*a*) yellow crystals (m.p. 170°) but containing no arsenic, and (*b*) a violet noncrystallisable compound containing arsenic. The identity of either compound could not be ascertained.



$$C_6H_6 + Cl_2As{\cdot}CH{:}CH\,Cl \rightarrow Ph{\cdot}As\,(Cl){\cdot}CH : CHCl$$

(I)

$$Ph_2{\cdot}As{\cdot}CH : CHCl$$

(II)

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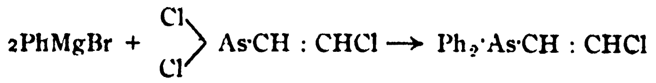
* Results of preliminary experiments were hopeful and the procedure to be adopted was published (*Proc. Indian Science Congress*, 1933, p. 169). Mannich (*Arch Pharm.*, 1935, **273**, 275), while studying the action of arsenic trichloride on 1-phenyl-3-diethylaminopropine, obtained two different types of compounds, one of them being a derivative of arsindole and took no notice of the publication referred to above and consequently a note was published by the author (*J. Indian Chem. Soc.*, 1935, **12**, 627).

The synthesis of secondary and tertiary arsines by the above method is not uncommon. Thus benzene and arsenic trichloride give primary and secondary arsines (*cf.* La Coste and Michaelis, *Ber.*, 1878, **11**, 1883; *Annalen*, 1880, **201**, 184). La Coste (*Inaug. Dissert.*, *Freiburg*, 1879) and Wieland (*Annalen*, 1923, **431**, 30) have shown that the Friedel-Craft's reaction may be used for the preparation of primary, secondary, and tertiary arsines, the yield of the last one being the maximum.

The analytical data of compounds (I) and (II) are in close agreement with the theoretically calculated figures. To corroborate further the correctness of the structure of the above compounds the following syntheses were effected :

$$\underset{}{PhMgBr} + \underset{(I)}{Ph{\cdot}As(Cl)CH : CH{\cdot}Cl} \longrightarrow \underset{(II)}{Ph_2{\cdot}As{\cdot}CH : CHCl}$$

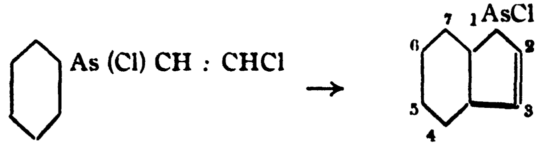


$$2PhMgBr + \begin{matrix} Cl \\ Cl \end{matrix}\!\!>As{\cdot}CH : CHCl \longrightarrow Ph_2{\cdot}As{\cdot}CH : CHCl$$

(II)

In each case a tertiary arsine has been obtained which readily gives a solid mercuric chloride double compound of the type $Ph_2As{\cdot}CH = CHCl, HgCl_2$ having identical properties.

The conversion of β-chlorovinylphenylchloroarsine into 1-chloroarsindole was effected by heating in dry carbon disulphide with aluminium chloride. The reaction is vigorous without any solvent and a reddish violet product of an indefinite nature is formed.



Besides the analytical data the correctness of the structure of 1-chloroarsindole was established by oxidising it with dilute nitric acid to *o*-carboxyphenylarsonic acid (*cf.* Lewis and Cheetham, *J. Amer. Chem. Soc.*, 1923, **45**, 510 ; Bert, *Annalen*, 1922, **429**, 86, 111 ; G. P. 250264 ; Aeschlimann and McCleland, *J. Chem. Soc*, 1924, **125**, 2025 ; Rosenmund, *Ber.*, 1921, **54**, 438). The *o*-carboxyphenylarsonic acid does not melt up to 320° and its identity with that obtained from the usual sources was proved by its conversion into oxide and also hydrolysing the oxide to benzoic acid.

EXPERIMENTAL.

Interaction of Benzene and β-Chlorovinyldichloroarsine.—The operation was conducted with or without aluminium chloride as follows:

(*i*) A mixture of β-chlorovinyldichloroarsine (30 g.), dry benzene (10 g.) and anhydrous aluminium chloride (7 g.) in a flask, fitted with condenser and calcium chloride guard tube, was allowed to stand for some time when there was evolution of hydrogen chloride with rise in temperature. The reaction was moderated by cooling the flask with ice-cold water. Occasionally application of heat was required to start the reaction. The deep brown reaction product was allowed to remain for 2 hours. It was next decomposed with cold dilute hydrochloric acid and the viscous brown product, thus obtained, was extracted first with ether and then with carbon tetrachloride. The extracts contained a violet solid which was removed. The ethereal extract was washed successively with cold dilute sodium carbonate solution, dilute hydrochloric acid and water, dried over calcium chloride. The solvent was nearly evaporated off, and the solution treated with ether when a precipitate was formed which was crystallised from acetone in needles, m.p. 170° (decomp.); as it contained no arsenic its identity was not sought for. It gives fluorescence with alcohol. The solvent was removed from the solution and the oil was fractionated, The principal fractions collected were at (*a*) 130-150°/5 mm. and (*b*) 180-200°/5 mm.

(*ii*) A mixture of benzene (25 c.c) and β-chlorovinyldichloroarsine (35 c.c.) was refluxed at 150-60° for 36 hours and the resulting product was extracted with ether and the ethereal solution was washed as described above and the oil obtained was fractionated. Two fractions were collected (1) at 128-148°/4 mm., (2) 178-195°/4 mm.

β-Chlorovinylphenylchloroarsine.—The fraction, b.p. 130-150/5 mm. was redistilled in *vacuo* through a long fractionating column when a light yellow product was obtained, b.p. 138-42°/3 mm. It was identified and proved to be analogous to the compound obtained from phenyldichloroarsine and acetylene (to be communicated later) by its conversion into the acid and determining the mixed m.p. The compound possesses an unpleasant odour but is not so irritant as the parent substance. [Found: C, 38·1; H, 2·5; Cl, 28·4; As, 30·3; M.W. (cryoscopic in benzene), 246·8. Calc. for $C_8H_7Cl_2As$: C, 38·5; H, 2·8; Cl, 28·5; As 30·12 per cent. M. W., 249].

β-Chlorovinyldiphenylarsine.—The fraction, b.p. 180-210°/5 mm., was redistilled at 190-98°/3 mm. as a yellow viscous oil. This was identified by its synthesis from bromobenzene and β-chlorovinyldichloroarsine:

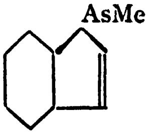
To the Grignard reagent from bromobenzene (15 g.), magnesium (2·4 g.) in absolute ether (100 c.c), β-chlorovinyldichloroarsine (10 g.) in dry ether was added drop by drop with shaking. The reaction mixture was heated for 1 hour on a water-bath, cooled and decomposed by ice-cold dilute hydrochloric acid. The ethereal layer was removed and the aqueous layer extracted with more ether. The extracts were washed successively with dilute sodium hydroxide solution, dilute hydrochloric acid and water and was dried over fused calcium chloride; the ether evaporated off in an atmosphere of carbon dioxide and the residual oil was distilled at 198-205°/3 mm. During distillation white fumes were evolved and solid particles were found to be deposited on the delivery tube. The distillate was turbid and it was found to be insoluble in alcohol. It was shaken with excess of alcohol, and the lower layer was removed, dissolved in ether and filtered. The ether from the filtrate was evaporated off and the liquid distilled. The fraction (small in quantity) up to 195°/3 mm. was collected separately and the main bulk distilled at 195-98°/3 mm. In a similar manner this compound was prepared from phenyl magnesium bromide and β-chlorovinylphenylchloroarsine.

It is a viscous yellow oil possessing slightly offensive odour. It causes blister on the skin. [Found: C. 57·6; H, 3·9; Cl, 12·5; As, 25·2; M.W. (cryoscopic in benzene), 288·9. $C_{14}H_{12}Cl$ As requires C, 57·8; H 4·1; Cl, 12·2; As, 25·8 per cent. M.W., 290·5].

β-Chlorovinyldiphenylarsine Mercuric Chloride.—On mixing molecular proportions of β-chlorovinyldiphenylarsine and mercuric chloride in ether a white precipitate appeared which was filtered off, finely powdered and washed with excess of ether. It was dissolved in chloroform and precipitated by ether and was crystallised from excess of alcohol, m.p. 238°. The mixed melting point of this compound and that prepared from benzene and β-chlorovinyldichloroarsine was also found to be 238°. (Found: Hg, 35·5. $C_{14}H_{12}Cl_3$ As Hg requires Hg, 35·6 per cent).

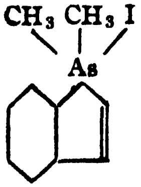
1-Chloroarsindole.—β-Chlorovinylphenylchloroarsine (22 g.) and anhydrous aluminium chloride (10 g.) were dissolved in absolute carbon disulphide and heated for 7 hours. The evolution of hydrogen chloride was slow and uniform throughout this period and the colour of the mixture changed to deep brown. On keeping the reaction mixture overnight, two layers separated, the lower one being deep brown in colour and the upper one colourless. The mixture was decomposed by dilute hydrochloric acid. The carbon disulphide layer was separated and the acid layer was extracted several times first with carbon tetrachloride and then with ether. The different extracts were filtered and the solvents evaporated off in an atmosphere of CO_2 under reduced pressure. The residual brown oil was distilled at 100-75°/6 mm. This was redistilled and the following fractions were collected: (*a*) 100-125°/3 mm. (light oil, 1 c.c.); (*b*) 130-145° (yellow oil, 63·5 c.c.). The fraction, b.p. 130-45°, was redistilled using a long fractionating column when a light yellow oil was obtained at 128-35°/3 mm. It has a very penetrating odour and has a very strong corrosive action on the skin. The compound is found to be soluble in the common organic solvents. It darkens when kept exposed to the action of light. [Found: C, 44·9; H, 2·7; Cl, 16·3; As, 35·5; M.W. (cryoscopic in benzene), 215; C_8H_6ClAs requires C, 45·1; H, 2·8; Cl, 16·7; As, 35·2 per cent. M.W., 212·5].

1-Methylarsindole.



To the magnesium compound from methyl iodide (4 g.) magnesium (0·6 g) and dry ether (40 c.c.), 1-chloroarsindole (5 g.) in ether was added drop by drop. The resulting mixture was heated on a water-bath for 3 hours and allowed to stand overnight. The mixture was decomposed with water and dilute hydrochloric acid. The yellow ethereal layer was removed and the coloured aqueous layer was extracted several times with ether till it was perfectly colourless. The ethereal solution was filtered and the ether evaporated off when a golden yellow oil was obtained possessing the characteristic smell of phenyl mustard oil. This was distilled at 142-45°/6 mm. [Found: C, 55·9; H, 4·8; As, 38·8; M.W. (cryoscopic), 189. C_9H_9As requires C, 56·2; H, 4·6; As, 39·06 per cent. M.W., 192].

1-Dimethyliodoarsindole.



1-Methylarsindole was heated for 1 hour on a water-bath with excess of methyl iodide, when crystals separated. The crystals were collected and crystallised from alcohol in yellow beautiful needles. It decomposes at 316-18° but does not melt upto 320°. (Found: As, 22·4. $C_{10}H_{12}IAs$ requires As, 22·4 per cent).

1-Methylarsindole Mercuric Chloride.—An ethereal solution of 1-methylarsindole was added to molecular proportion of mercuric chloride in the same solvent The white precipitate was repeatedly washed with ether, dried and crystallised from alcohol in white silky needles, m.p. 150-51°. (Found: Hg, 43·03. $C_9H_9Cl_2As$ Hg requires Hg, 43·1 per cent).

Oxidation of 1-Chloroarsindole.—1-Chloroarsindole was treated with excess of dilute nitric acid (60%). When the vigorous reaction subsided the reaction mixture was heated to dryness on a water-bath. The residue was dissolved in dilute sodium hydroxide solution and *o*-carboxyphenylarsonic acid was precipitated by dilute hydrochloric acid as a colourless solid. It was crystallised from water as colourless glistening plates, not melting up to 320°. It was converted into oxide by reducing the aqueous solution of the acid by SO_2 and HI at 60° and also hydrolysing the oxide to benzoic acid.

My thanks are due to Dr. M. Goswami and to Mr. B. C. Ray for their keen interest in this investigation.

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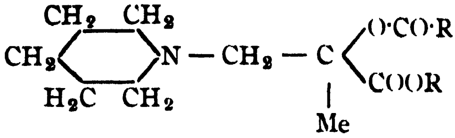
Received February 17, 1937.

SYNTHESIS OF NEW LOCAL ANÆSTHETICS. PART II.

By Kidar Nath Gaind, Abdul Wahab Khan and Jnanendra Nath Rây.

In part I of this series (*J. Indian Chem. Soc.*, 1937, **14**, 13) some esters of α-acyloxy-β-aminoalkyl*iso*butyric acid have been described which are endowed with local anæsthetic property. In the present investigation we have synthesised some compounds possessing the following general formula:

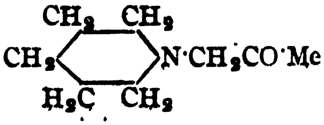


(I)

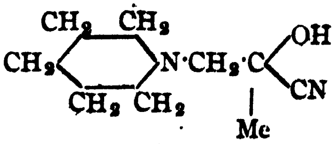
The starting material was α-hydroxy-β-chloro*iso*butyric acid described in Part I.

The α-hydroxy-β-chloro*iso*butyric acid was first esterified with various alcohols (ethyl, propyl, *iso*propyl and benzyl alcohols) and the resulting esters were heated with piperidine in dry benzene solution under pressure at 100°. The crude condensation products (unpurifiable liquids) were directly acylated with benzoyl chloride or *p*-nitrobenzoyl chloride. The hydrochloride of the acylated base (I) was purified and the products in the case of *p*-nitrobenzoyl derivatives were further reduced to the corresponding aminobenzoyl derivatives.

An alternative scheme was followed in which chloroacetone was condensed with piperidine to get piperidinoacetone previously described by Stoermer and Burkert (*Ber.*, 1895, **28**, 1200). It formed a bisulphite compound, which reacted with potassium cyanide solution to give β-piperidino-α-hydroxy*iso*butyronitrile (III). The hydrolysis of the nitrile with acids did not succeed as the substance decomposed into piperidine and the aliphatic component when the ester hydrochloride was treated with mildest of alkali.



(II)



(III)

The products described in the paper have strong local anæsthetic property, the toxicity and other details are being investigated at the King George Medical College, Lucknow A full account of these will appear elsewhere.

EXPERIMENTAL.

Ethyl α-Benzoyloxy-β-piperidinoisobutyrate. — Ethyl β-chloro-α-hydroxy*iso*butyrate (8 g., b.p. 85°/11 mm.) (*cf.* Fourneau "Organic Medicaments," 1925, p. 222) and piperidine (8·2 g.) was heated in benzene solution (50 c.c.) under pressure at 100° for 6 hours. After the removal of precipitated piperidine hydrochloride, the filtrate was washed with water, dried, solvent removed and the residue (5·5 g.) was directly heated with benzoyl chloride (5 g.) in toluene solution for 3 hours on an oil-bath. The cooled product was left at 0° for 12 hours. The separated solids were filtered and washed with dry ether and finally crystallised from hot acetone in needles, m.p. 128°. (Found : N, 3·95 ; Cl, 10·28. $C_{18}H_{26}O_4NCl$ requires N, 3·94 ; Cl, 9·98 per cent).

Hydrochloride of Ethyl α-p-Nitrobenzoyloxy-β-piperidinoisobutyrate.—(I, $R = Et$, $R' = C_6H_4 \cdot NO_2$).—A mixture of *o*-nitrobenzoyl chloride (9 g.), ethyl α-hydroxy-β-piperidino*iso*butyrate (8·6 g.) and toluene (100 c.c.) was heated on the oil-bath for 2½ hours. The product was isolated as described before. The *hydrochloride* crystallised from acetone—alcohol or from hot acetone in needles, m.p. 76°, yield 14·7 g. The substance crystallised with a molecule of acetone. (Found : N, 6·21 ; Cl, 7·4. $C_{18}H_{25}O_6N_2Cl$, C_3H_6O requires N, 6·1 ; Cl, 7·7 per cent). The substance on heating gives off acetone which was qualitatively tested and established. [Found (in the material dried in high vacuo at 68°) : N, 6·75 ; Cl, 8·5. $C_{18}H_{25}O_6N_2Cl$ requires N, 6·9; Cl, 8·8 per cent).

Ethyl α-p-Aminobenzoyloxy-β-piperidinoisobutyrate.—The foregoing nitro ester hydrochloride (5 g.) was catalytically reduced in alcohol with platinum oxide and hydrogen. The solution after reduction was filtered and three-fourths of this solvent removed in *vacuo*. The residue was left in *vacuo*. After three days, crystallisation was complete. The product was washed with dry ether. It could not be satisfactorily recrystallised as considerable loss of material occurs, m.p. 102°. (Found : Cl, 9·1. $C_{18}H_{27}O_4N_2Cl$ requires Cl, 9·5 per cent).

Propyl α-Benzoyloxy-β-piperidinoisobutyrate.—The acid (15 g.) was esterified with propyl alcohol in the usual manner, b.p. 120°/15 mm. (Found : Cl, 19·49. $C_7H_{13}O_3Cl$ requires Cl, 19·6 per cent). A mixture of the foregoing ester (9·8 g.), piperidine (10 g.) in benzene was heated under pressure as described before. The crude product was benzoylated by heating with benzoyl chloride in toluene solution. The *hydrochloride* (I, R = C_3H_7, R′ = Ph) was crystallised from acetone-ether mixture, m.p. 115°. (Found : Cl, 9·8. $C_{19}H_{28}O_4NCl$ requires Cl, 9·6 per cent).

The preparation of (I, R = *iso* C_3H_7, H in place of R′CO).—*iso*Propyl β-chloro-α-hydroxy*iso*butyrate (*cf.* Part I) (9·3 g.), piperidine (9 g.) in dry benzene (5 c.c.) was heated at 100° under pressure for 6 hours. The precipitated piperidine hydrochloride was removed and the benzene solution well washed with water, dried and the solvent removed. The residual oil in ether was converted into the hydrochloride by ethereal hydrogen chloride and the precipitated solids were crystallised from a mixture of ether and alcohol, m.p. 115°. (Found : Cl, 13·6. $C_{12}H_{24}O_3NCl$ requires Cl, 13·4 per cent).

Hydrochloride of iso*Propyl* α- *Benzoyloxy*-β- *piperidino*iso*butyrate* (I, R′ = Ph, R = *iso*-C_3H_7) was converted into the free ester (2 g.) and was heated with benzoyl chloride (1·5 g.) at 130° for 1 hour. After cooling the reaction mixture was kept in contact with dry ether at 0° for 12 hours. The solids were collected and crystallised from a mixture of hot acetone and ether, m.p. 156°. (Found : Cl, 9·32. $C_{19}H_{28}O_4NCl$ requires Cl, 9·6 per cent).

Hydrochlorde of iso*Propyl* p-*Nitrobenzoyloxy*-β-*piperidino*iso*butyrate*.—*p*-Nitrobenzoyl chloride (5 g.) in dry toluene (50 c.c.) was heated with *iso*propyl ; α-hydroxy-β-piperidino *iso*butyrate (5·1 g.). The product, isolated as described before, was crystallised from a mixture of acetone and alcohol in needles. m.p. 61°. (Found : N, 6·54; Cl, 8·30. $C_{19}H_{27}O_6N_2Cl$ requires N, 6·76 ; Cl, 8·56 per cent).

The foregoing nitro compound was reduced with platinum oxide catalyst as described before but the product could not be satisfactorily recrystallised as it was extremely hygroscopic.

*Hydrochloride of Benzyl α-Benzoyloxy-β-piperidino*iso*butyrate*.—Benzyl β-chloro-α-hydroxy*iso*butyrate (*cf.* Part I) (7 g.) and piperidine (5·5 g.) was condensed and the product isolated in the usual manner. The crude product (1 g.) and benzoyl chloride (0·7 g.) were heated at 150° for 2-3 hours. The semi-solid mass obtained after the addition of ether, solidified on keeping at 0° for 2 weeks. It was recrystallised from a mixture of ether and alcohol, m.p. 195-97°. (Found : Cl, 8·7. $C_{23}H_{28}O_4NCl$ requires Cl, 8·5 per cent).

Piperidinoacetone was prepared by the method of Stoermer and Burkert (*loc. cit.*). (Oxime, m.p. 104° ; phenylhydrazone, m.p. 63°).

β-Piperidino-α-hydroxyisobutyronitrile.—Piperidinoacetone (13 g.) was shaken with a solution of sodium hydrogen sulphite (18 g. in 18 c.c. of water) in the cold. A solution of potassium cyanide (10 g. in 10 c.c. of water) was added with shaking, the temperature was not allowed to exceed 5°. The separated oil was extracted with ether and then the solvent removed, yield 6·5 g. It decomposes on distillation under reduced pressure. The foregoing nitrile was hydrolysed to the ester in absolute alcoholic solution with hydrogen chloride by boiling for 1½ hours. On treatment with sodium carbonate solution the ester hydrochloride decomposed into piperidine and ethyl αβ-dihydroxy*iso*butyrate.

One of us (K.N.G.) is indebted to the Lady Tata Trust for a scholarship which enabled him to take part in this investigation.

THE UNIVERSITY CHEMICAL
LABORATORIES, LAHORE

Received February 20, 1937.

INDIGOID VAT DYES OF THE ISATIN SERIES. PART II. 3-INDOLE-2'-(6'-METHYL)-THIONAPHTHENEINDIGOS.

BY SISIR KUMAR GUHA.

It has been found from a study of the tinctorial properties of 2-(5-methyl) thionaphthene-acenaphthylene-indigos (Guha, *J. Indian Chem. Soc.*, 1933, **10**, 679) and those of the corresponding 2-(6-methyl) derivatives (Guha, *ibid.*, 1936, **13**, 94) that Martinet's rule (*Rev. Gen. Mat. Col.*, 1921, **25**, 17) is applicable to 2-thionaphthene-acenaphthylene indigos (Bezdzik and Friedlander, *Monatsh*, 1908, **29**, 386; E. P. 344/08; G. P. 226244; Mayer and Schönfelder, *Ber.*, 1922, **55**, 2972; G. P. 213504; E. P 20003/08; Guha, *J. Indian Chem. Soc.*, 1932, **9**, 423) as far as one methyl group in the thionaphthene part of the molecule is concerned. Further, Guha and Basu-Mallik prepared 3-indole-2'-(5'-methyl)-thionaphthene indigos (*J. Indian Chem. Soc.*, 1934, **11**, 395) and showed that these indigoid dyes impart deeper shades on cotton and on wool than those of the 2-(5-methyl)-thionaphthene-acenaphthyleneindigos (Guha, *loc. cit.*).

In view of these observations, the present work was undertaken with the object of preparing 3-indole-2′-(6′-methyl)-thionaphtheneindigos and comparing them with those of the corresponding 5′-methyl derivatives (Guha and Basu-Mallik, *loc. cit.*). It was also intended to examine how far Martinet's rule is obeyed by 3-indole-2′-thionaphthene indigo, commercially known as Thioindigo Scarlet R (Bezdzik and Friedlander, *Monatsh.*, 1908, **29**, 376; E. P. 17162/06; G. P. 241327) and its derivatives (Ciba Red G, etc., E. P. 19158/07 and G. P. 277358) having one methyl group present in the thionaphthene nucleus of the molecule.

6-Methyl-3-hydroxythionaphthene (Friedlander, **9**, 589; Auwers and Thies, *Ber.*, 1920, **53**, 2293) has, therefore, been condensed with isatin, 5-chloro-, 5-bromo-, 5:7-dibromo-, 5-bromo-7-nitro-, and 5:7-dinitroisatin and the corresponding vat dyes obtained easily. All of them when rubbed develop a beautiful lustre, although not coppery like ordinary indigo. This property is also exhibited by the corresponding 5′-methyl derivatives (Guha and Basu-Mallik, *loc. cit.*) now studied by the present author for comparison. They resemble the corresponding 5′-methyl derivatives in solubility, in the action of heat above 310° and in the action of cold concentrated sulphuric acid in producing characteristic colouration. Most of these dyes possess well-developed dyeing properties. All of them dye wool from an acid bath producing uniformly and fully developed shades. They dissolve in alkaline hydrosulphite giving vats, the colours of which are similar to those of the corresponding 5′-methyl compounds, and from these vats the original dyes are reprecipitated on oxidation. The colours imparted on cotton by the mother compound, its chloro, and bromo derivatives are slightly lighter than those of the shades of the original substances but in case of dibromo, bromonitro, and dinitro derivatives uniform deep shades have been obtained.

These 3-indole-2′-(6′-methyl)-thionaphtheneindigos are decisively much lighter in colour than the analogously composed 5′-methyl derivatives (Guha and Basu-Mallik, *loc. cit.*), a result in conformity with Martinet's rule. It has also been found that the 6′-methyl dyes obtained from isatin, 5-chloro-, and its 5-bromo derivatives developed colours on cotton and on wool which are deeper than those of the nearly corresponding 6-methyl-compounds in the acenaphthenequinone series [*cf.*, 2-(5-methyl)-thionaphthene-acenaphthyleneindigos and 3-indole-2′-(5′-methyl)-thionaphthene-indogos, Guha and Guha and Basu-Mailik, *loc. cit.*].

The colours obtained from the dyes mentioned in this paper and those from the corresponding $5'$-methyl derivatives (Guha and Basu-Mallik, *loc. cit.*), are compared in the following table.

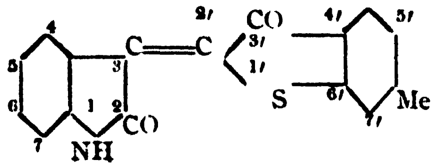
Substances.	Colour on wool	Colour on cotton.
3-Indole-2'-(6'-methyl)-thionaphthene-indigo	Red	Light red
3-Indole-2'-(5'-methyl)-thionaphthene-indigo	Brilliant scarlet red	Light red
3-(5-Chloro)-indole-2'-(6'-methyl)-thionaphtheneindigo.	Red	Red
3-(5-Chloro)-indole-2'-(5'-methyl)-thionaphtheneindigo.	Scarlet red	Scarlet red
3-(5-Bromo)-indole-2'-(6'-methyl)-thionaphtheneindigo.	Red	Red
3-(5-Bromo)-indole-2'-(5'-methyl)-thionaphtheneindigo.	Scarlet red	Scarlet red
3-(5 :7-Dibromo)-indole-2'-(6'-methyl)-thionaphtheneindigo.	Light scarlet red	Scarlet red
3-(5 :7-Dibromo)-indole-2'-(5'methyl)-thionaphtheneindigo	Deep red	Deep red
3-(5-Bromo-7-nitro)-indole-2'-(6'-methyl)-thionaphtheneindigo.	Red	Dark red
3-(5-Bromo-7-nitro)-indole-2'-(5'-methyl)-thionaphtheneindigo.	Dark red	Dark red
3-(5 :7-Dinitro)-indole-2'-(6'-methyl)-thionaphtheneindigo.	Blood red	Dark red
3-(5 :7-Dinitro)-indole-2'-(5'-methyl)-thionaphtheneindigo.	Dark red	Dark red

Further work for studying the preparation and properties of 3-indole-2'-(4'-methyl)-thionaphtheneindigos has been undertaken.

EXPERIMENTAL.

The indigoid dyes have been prepared by a method similar to that described by Guha and Basu-Mullik (*loc. cit.*) for the preparation of 3-indole-2'-(5'-methyl)-thionaphtheneindigos.

3-Indole-2'-(6'-methyl)-thionaphtheneindigo.



It was prepared from isatin (0·735 g.) and 6-methyl-3-hydroxythionaphthene (0·82 g.) in 60 c.c. of glacial acetic acid and 4 c.c. of concentrated hydrochloric acid. It separated in silky scarlet bundles of sharp needles. The product (1·194 g.) crystallised from glacial acetic acid in silky red crystals. It is moderately soluble in benzene, acetone and chloroform. It dyes wool in red shades from an alkaline hydrosulphite vat. (Found : S, 11·33. $C_{17}H_{11}O_2NS$ requires S, 10·92 per cent).

3-(5-*Chloro*)-*indole*-2'-(6'-*methyl*)-*thionaphthencindigo* separated as long red needles by the condensation of 5-chloroisatin (0·544 g.) and 6-methyl-3-hydroxythionaphthene (0·492 g.) in 115 c.c. of acetic acid and 5 c.c. of concentrated hydrochloric acid. The dye (0·864 g.) crystallised from pyridine in clusters of deep red needles. It dyes both wool and cotton in red shades. (Found : Cl, 10·85. $C_{17}H_{10}O_2NClS$ requires Cl, 10·83 per cent).

3-(5-*Bromo*)-*indole*-2'-(6'-*methyl*)-*thionaphthencindigo* was obtained as long silky red needles by reacting 5-bromoisatin (0·452 g.) and 6-methyl-3-hydroxythionaphthene (0·328 g.) in 75 c.c. of acetic acid and 5 c.c. of concentrated hydrochloric acid. The substance (0·652 g.) was crystallised from pyridine in fibre-like deep red long needles when it lost its silky lustre. The dyeing shades on wool and on cotton are similar to those of the chloro compound but is slightly deeper in each case. (Found : Br, 21·13. $C_{17}H_{10}O_2NBrS$ requires Br, 21·51 per cent).

3-(5:7-*Dibromo*)-*indole*-2'-(6'-*methyl*)-*thionaphthencindigo* separated from 5:7-dibromoisatin (0·61 g.) and the methylhydroxythionaphthene (0·328 g.) in 100 c.c. of acetic acid and 5 c.c. of concentrated hydrochloric acid in deep red fibre-like small needles. The dye (0·819 g.) crystallissd from nitrobenzene in beautiful foliated needles. It dissolves in strong sulphuric acid with an olive-brown colour. It dyes wool in light scarlet-red shades and cotton in scarlet-red shades. (Found : Br, 35·39. $C_{17}H_9O_2NBr_2S$ requires Br, 35·47 per cent).

3-(5-*Bromo*-7-*nitro*)-*indole*-2'-(6'-*methyl*)-*thionaphtheneindigo* was prepared from 5-bromo-7-nitroisatin (0·813 g.) and 6-methyl-3-hydroxy-thionaphthene (0·492 g.) in 95 c.c. of glacial acetic acid and 6 c.c. of concentrated hydrochloric acid. The light scarlet-red substance (1·099 g.) separated from pyridine in fine hair-like needles. It dissolves in strong sulphuric acid with a yellowish-green colour. It dyes wool in red shades and cotton in dark red shades. (Found : Br, 19·43. $C_{17}H_9O_4N_2BrS$ requires Br, 19·18 per cent).

3-(5:7-*Dinitro*)-*indole*-2'-(6'-*methyl*)-*thionaphtheneindigo*.—The dark red crystalline precipitate (0·692 g.), obtained from 6:7-dinitroisatin (0·474 g.)

and 6-methyl-3-hydroxythionaphthene (0·328 g.) in 65 c.c. of acetic acid and 3—4 c.c. of concentrated hydrochloric acid, separated from pyridine in fine needles. It dissolves in strong sulphuric acid with an olive-brown colouration. It dyes wool in blood-red shades and cotton in dark red shades. (Found : S, 8·45. $C_{17}H_9O_6N_3S$ requires S, 8·35 per cent).

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PATNA.

Received February 25, 1937.

REVIEWS.

Official and Tentative Methods of Analysis of the Association of Official Agricultural Chemists, FOURTH EDITION, 1935. PUBLISHED BY THE ASSOCIATION OF OFFICIAL AGRICULTURAL CHEMISTS AT WASHINGTON D. C. PP. 710. PRICE $5·50 (FOREIGN).

" The fourth issue*** is presented***to the public in accordance with the plan to publish a revision every five years.***

The general arrangement of subject matter follows the plan adopted for the second and third editions. Certain unsatisfactory methods have been omitted ****. The methods for beers, wines and distilled liquors, which constitute Chapter XVII in the third edition, have been assembled in three chapters entitled, respectively, Malt Beverages, Sirups and Extracts, and Brewing Materials ; Wines ; and Distilled Liquors. Two chapters of the third edition, *i.e.*, XIII Fibres, and XIV Paper and Paper Materials, have been deleted because at the present time the work on the materials is not considered to be of sufficient importance to enough members of our Association to warrant co-operative referee work, and further because such methods are being satisfactorily studied elsewhere.

Attention is called to a few of the additions to the methods which have special significance. In Chapter I, Soils, the method for the determination of selenium is timely, as is also the method for the determination of the acid-forming and non-acid-forming quality of fertilizers, in Chapter II, Fertilizers, because these subjects have assumed special importance during the last two years. The method for the determination of the phenol coefficient of disinfectants, included in Chapter VI on Insecticides and Fungicides, is an example of a departure into a field of more unusual methods. Chapter XII, Plants, has been materially revised and enlarged, and now includes a method for the determination of lignin. Methods have also been added under the chapter heading 'Nuts and Nut Products.'

The method for the determination of lead given in the chapter on Baking Powders has been deleted. Only the comprehensive method for lead in Chapter XXIX, Metals in Foods, has been included. The vitamin D assay by preventive biological test in Chapter XXVII, Grain and Stock Feeds, should be noted, as should also the revised and rearranged Chapter XXXIV, Sugars and Sugar Products.

Another innovation which should later make a valuable addition to the book is Appendix I, which presents methods for the preparation and standardization of solutions. At present only procedures for hydrochloric acid and alkali are given, but with the appointment of a referee on this subject other material will soon be available. A revised and enlarged section on definitions of terms and interpretation of results on fertilizers and liming materials constitutes Appendix II."

The above extracts taken from the preface indicate the main additions and alterations made in the present edition as compared with the previous edition. This standard publication needs no introduction and the present edition will be found as authoritative and useful as, if not more than, its predecessors. It will perhaps be useful even at the expense of making this review lengthy to indicate the additions and alterations in some detail.

Chap. I. Methods of determination of arsenic and selenium have been added. The method of determination of iodine has been described in more detail.

Chap. II. Methods of determination of moisture by distillation with toluene, water insoluble nitrogen in cyanamide, total magnesia and acid-forming and non-acid-forming quality fertilizers, have been added. The chapter has been rearranged.

Chap. VI. A method of determination of phenol coefficients of disinfectants has been added.

Chap. VIII. The sections on rosin and turpentine oil have been enlarged.

Chap. IX. Sections on oleoresinous varnishes, raw linseed oil and boiled linseed oil have been added.

Chap. XII. Methods of determination of sodium and potassium, iodine, selenium, ammonia in tobacco, free nicotine in tobacco and lignin have been added. The chapter has been revised and considerably enlarged.

Chap. XVI. The section on methyl alcohol has been enlarged and a sub-section under 'Cordials and Liquors' added.

Chap. XVII. The sections on lead and fluorides have been omitted.

Chap. XIX. A section on silver number of detection of cocoanut and palm kernel oils has been added.

Chap. XX. Sections on benzoyl peroxide bleach in flour, detection of rye flour in wheat flour, diastatic activity of flour, viscosity of acidulated flour and milk solids in bread have been added. The chapter has been considerably enlarged.

Chap. XXII. Sections on sediment test, lactose in process cheese and gums in cheese have been added.

Chap. XXIII. Methods of determination of dextrose and sucrose and glycerol and sections on acidity of ether extract and ammonia nitrogen have been added.

Chap. XXVI. Sections on lævo-malic acid and inactive malic acid have been added.

Cnap. XXVII. Sections on protein, cyanogenetic glucosides in feeds and similar materials have been enlarged and a section on vitamin D assay by preventive biological test has been added.

Chap. XXIX. The sections on arsenic and lead have been enlarged and a section on mercury has been added.

Chap. XXX. It is a new chapter.

Chap. XXXI. A section on cotton seed has been added.

Chap. XXXIII. The section on volatile oil has been enlarged.

Chap. XXXVII. A sub-section on flourides under 'Potable Waters' has been added.

Chap. XXXVIII. A gama ray method has been added.

Chap. XXXIX- The sections on elixir of terpene hydrate, ipomea, jalap, podophyllum and aloin have been added and the section on bio-assay of drugs has been enlarged.

An appendix on standard solutions has been added.

J. N. M.

Drilling Mud; Its Manufacture and Testing By P. EVANS, M.A., F.G.S., M. INST. P.T. AND A. REID, M.A., A.M. INST. P.T. PUBLISHED BY THE MINING AND GEOLOGICAL INSTITUTE OF INDIA, CALCUTTA. PP. 263. PRICE RS. 13 OR 19*s*. 6*d*. (INCLUDING POSTAGE).

The work under review forms volume XXXII of the Tiansactions of the Mining and Geological Institute of India. It is divided into parts :—Part I dealing with the manufacture, maintenance and reconditioning of 'drilling mud' and Part II with the testing and the study of its various physical properties. These properties include specific gravity, viscosity, thixotropy, surface tension, stability, salinity, acidity and alkalinity, size of the particles and plastering power. One of the most important properties of drilling mud is its viscosity, about which much confusion exists in the literature both regarding measurement and interpretation of results. The authors have discussed this subject very comprehensively and have emphasised, very correctly indeed, on the necessity of recognising at least two factors, *viz.*, the 'yield value' and the 'mobility' in the determination of resistance to flow of mud fluid through narrow tubes. Thixotropy is a phenomenon of fairly common occurrence in drilling mud and when a thixotropic 'sol' sets to 'gel', the process is accompanied by changes in viscosity. This phenomenon and its possible bearing on the variable viscosity observed in plastic flow have also received careful treatment in this paper. The text is well illustrated and the references cover a wide range of relevant literature. The detailed lists of contents and the complete indices make it easy to turn to any of the subjects dealt with. The paper furnishes a good example as to how a problem of purely scientific research can yield results having important technical application.

The Editor of the Transactions of the Mining and Geological Institute of India will welcome contribution to the discussion of the paper reviewed. The volume can be had from

The Publisher, 27, Chowranghee, Calcutta, India.

and

The Institution of Petroleum Technologists, Aldine House, Bedford Street, Strand, London W.C. 2.

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OXIDATION OF SULPHYDRYL BODIES BY HYDROGEN PEROXIDE IN PRESENCE OF INORGANIC CATALYSTS.

PART II. OXIDATION OF CYSTINE BY MEANS OF HYDROGEN PEROXIDE IN PRESENCE OF VANADIC ACID SOL.

By J. C. Ghosh and B. C. Kar.

In a previous paper (*J. Indian Chem. Soc.*, 1934, **11**, 485) the oxidation of cystine and dithiodiglycollic acid by means of hydrogen peroxide in presence of tungstic acid and molybdic acid sols has been described. Oxidation of cystine by means of hydrogen peroxide can also be carried out in presence of vanadic acid sol. Cysteic acid has been isolated as the main product of oxidation. Ammonia, sulphuric acid and carbon dioxide in small quantities have also been detected.

EXPERIMENTAL.

Cysteic Acid.

Cystine (2·5 g.) was dissolved in minimum quantity of pure strong hydrochloric acid and 100 c.c. of redistilled water were added. Hydrogen peroxide was added in slight excess, one molecule of cystine requiring five molecules of hydrogen peroxide to form cysteic acid. 0·05*M*-sodium tungstate (2 c.c.) in the form of sol was then added and the reaction mixture was kept at room temperature (28-30°) with occasional shaking. After a few days when all the cystine was oxidised as shown by its absence when tested with uric acid reagent, the reaction mixture was evaporated slowly in a vacuum desiccator containing sulphuric acid at room temperature. Fine crystals of cysteic acid were obtained which were removed when completely dry by extracting with absolute alcohol and recrystallised from water in a desiccator.

Estimation of Carbon Dioxide.—Carbon dioxide was estimated by the following arrangements as shown in Fig. 1.

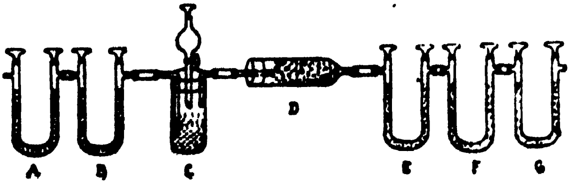


Fig. 1.

A and B are two glass stoppered U-tubes filled with soda lime to absorb atmospheric carbon dioxide and C is the reaction chamber fitted with a rubber cork through which the inlet and outlet tubes and a small glass stoppered separating funnel pass. D and E contain calcium chloride to absorb moisture. F and G are two other glass stoppered U-tubes containing soda lime. In F carbon dioxide from the reaction chamber is absorbed. G is the guard tube. All the tubes are joined by means of pressure tubes and made air-tight by coating the joints with paraffin wax.

Cystine solution (8 c.c.) in hydrochloric acid containing 0·25 g. cystine and hydrogen peroxide solution (5 c.c.) containing peroxide 1·5 times the theoretical amount to form cysteic acid were placed in the reaction chamber and tightly filled. Air was then drawn through the whole apparatus for 1 hour at a slow rate by means of an aspirator to remove the carbon dioxide initially present in the reaction chamber. The soda lime tube F was then very accurately weighed. Freshly prepared sol (2 c.c.) containing 1 c.c. 0·1*M* sodium tungstate was then introduced through the separating funnel and shaken by bubbling air for a few minutes and allowed to stand at room temperature for 36 hours. After that period carbon dioxide was absorbed in F by drawing air for three hours. On weighing the tube an increase in weight (4·3 mg.) was obtained. The control experiment similarly carried out but without the sol gave an increase in weight of only 0·3 mg.

Ammonia and Sulphuric Acid.—Ammonia and sulphuric acid can be easily detected in the reaction mixture, the former by Nessler's reagent and the latter by barium chloride, keeping suitable control. 0·2 G. of cystine gives about 1 mg. of ammonia after 48 hours.

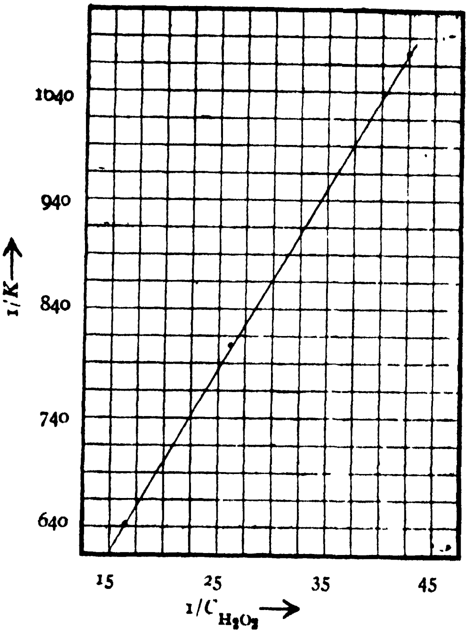
Kinetics of Reaction.

The methods of investigation are exactly the same as in the case of tungstic acid and molybdic acid sols (*cf.* Ghosh and Kar, *loc. cit.*). The sol was prepared by the addition of dilute hydrochloric acid to chemically pure sodium vanadate a few minutes before the experiment was begun.

$$4NaVO_3 + 2HCl = Na_2O, 2V_2O_5 + 2NaCl + H_2O.$$

No spontaneous decomposition of hydrogen peroxide took place at low concentration of the sol used, The sol itself liberates iodine from a solution of potassium iodide in sulphuric acid. It has been found that the total amount of iodine liberated by a mixture of sol and hydrogen peroxide is equal to the sum of the two liberated separately.

FIG. 2.



A correlation was, therefore, made in every experiment for the iodine liberated by the sol. The results of kinetic measurements are given below. In all the experiments the concentration of sol is expressed in terms of $NaVO_3$. Table I gives a typical experiment in detail. The velocity is represented by a unimolecular equation of the form,

$$K = \frac{1}{t_2 - t_1} \log \frac{a - x_1}{a - x_2} .$$

TABLE I.

Conc. of H_2O_2 = 0·0385*M*. Cystine = 0·00417*M*. $NaVO_3$ = 0·001*M*. p_H = 1·15. Volume = 15 c.c. Temp. = 31°. Composition of the reaction mixture: 3 c.c. of cystine + 6 c.c. of HCl + 3 c.c. of sol + 3 c.c. of H_2O_2.

	Time.	0·01*N*-thio ≡ 0·504 c.c. of reaction mixture.	*K*.
	0 min.	3·92 c.c.	
1.	4	3·89	0·0012 (1 & 2)
2.	43	3·68	0·0012 (2 & 3)
3.	88·5	3·46	0·00125 (3 & 4)
4.	128·5	3·28	0·0013 (4 & 5)
5.	172·5	3·10	0·00125 (5 & 6)
6.	231·5	2·90	
			Mean 0·00124

TABLE II.

Effect of varying the concentration of cystine.

Temp. = 31°. $p_H = 1·15$. $NaVO_3 = 0·001\ M$.

Initial conc. of cystine.	Conc. of H_2O_2.	K (mean).
0·00417 *M*	0·06*M*	0·00156
0·00834	0·06	0·00108
0·01251	0·058	0·00091

TABLE III.

Effect of varying the concentration of H_2O_2.

Temp. = 31°. Cystine = 0·00417*M*. $NaVO_3 = 0·001M$.

	$p_H = 1·56$.			$p_H = 1·15$.		
Initial conc. of $H_2O_2(M)$ ...	0·0236	0·0481	0·0776	0·0236	0·0385	0·06
K ...	0·0008	0·00085	0·00095	0·00093	0·00124	0·00156

When 1/*K* is plotted graphically against 1/conc. of hydrogen peroxide a straight line is obtained (*cf.* Fig. 2).

TABLE IV.

Effect of varying the concentration of $NaVO_3$.

Temp. = 31°. $p_H = 1·56$.
Cystine = 0·00417*M*.

Conc. of H_2O_2.	Conc. of $NaVO_3$.	*K*.
0·0224*M*	0·0005 *M*	0·0004
0·0236	0·001	0·0008
0·0243	0·002	0·0015

TABLE V.

Effect of varying the temperature.

$p_H = 1·56$. Cystine = 0·00417*M*.
$NaVO_3 = 0·001M$.

Temp.	Conc. of H_2O_2.	*K*.
21°	0·0253 *M*	0·00037
31°	0·0236	0·00080

TABLE VI.

Effect of varying the p_H.

Temp. = 31°. Cystine = 0·00417*M*. $NaVO_3$ = 0·001*M*.

$H_2O_2(M)$	...	0·0236	0·0236	0.0243
pH	...	1·15	1·56	2·3
K	...	0·00093	0·0008	0·00026

Sodium tungstate and ammonium molybdate also catalyse the oxidation of cystine by means of hydrogen peroxide. But unlike them pure sodium vanadate is not capable of catalysing the reaction.

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THERMOAGEING OF COLLOIDS. PART II. VARIATION OF THE VISCOSITY AND OPACITY.

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In a previous communication (Joshi and P. V. J. Rao, *J. Indian Chem. Soc.*, 1936, **13**, 217) results were recorded for change in μ_D, the refractive index produced by *thermoageing* some 19 colloids at different concentrations. In view of the fact that changes in viscosity and opacity have been widely employed to measure the corresponding degree of coagulation produced (for evidence to the contrary, *cf.* Joshi and co-workers, *vide infra*) and the possible analogy between '*ageing*' and coagulation it was considered desirable to examine the influence of 'thermoageing' on the above properties. It may also be mentioned that while the previous work on 'thermoageing' has been designed chiefly to study it in relation to coagulation (Davies, *J. Phys. Chem.*, 1929, **33**, 274), detailed data are not available in the literature for changes in the more important physical properties consequent on 'thermoageing', with the exception perhaps of an earlier paper from these laboratories (*loc. cit.*).

EXPERIMENTAL.

The colloid solutions of As_2S_3, MnO_2, Sb_2S_3, Fe_2O_3 and Prussian blue were prepared and their colloid contents estimated as described in Part I (*loc. cit.*); that of HgS was prepared by adding, in small quantities and with repeated shaking, from H_2S water to $N/10$-$Hg(CN)_2$ solution, until just a trace of the gas was perceptible. It was found that the colloid showed sensible coagulation on standing for about 10 days. The *thermoageing* experiments were, therefore, carried out with a fresh sol. The molybdenum blue was prepared by reducing with H_2S an acidified (with H_2SO_4) solution of ammonium molybdate, while boiling hot. The excess of H_2S was next removed by a current of hydrogen and the sol rendered electrolyte-free by dialysis. Selenium sol was prepared by reducing with a stream of SO_2 with continuous shaking, a solution of about 1 g. of SeO_2 in 500 c.c. of water after addition of about 20 c.c. of gelatine Before reduction the solution was warmed to 50°. The stability of the colloid was such that just slight sedimentation ensued after about a month. Colloidal vanadous acid was prepared by dispersing a small amount of V_2O_3 by repeatedly taking it up with water. About 10 % aluminium acetate was added drop by drop to boiling water with continuous shaking till the faint smell of acetic acid was just perceptible. This was next boiled for about 15 minutes, when the smell of the acid disappeared. The Al_2O_3 sol, thus obtained, was quite clear and stable. Suspensions of the linseed and *til* oil were prepared by the precipitation method described by Joshi (*Kolloid Z.*, 1923, **34**, 197; *cf.* also, *J. Bombay Univ.*, 1935, **4** 140).

A definite volume measured at a fixed temperature of each of the above sols was 'thermoaged' by refluxing it on a water-bath for 24 hours (except in the case of colloidal HgS, selenium and Al_2O_3 for which the times were shorter). A very slight reduction of volumes occurred in some cases, which was made up by adding the appropriate quantity of twice distilled water.

The viscosity (relative to that of water at the same temperature taken as untiy) of a sample before and after 'thermoageing' was measured by Scarpa's method with the modifications described previously (Joshi and Viswanath, *J. Indian Chem. Soc.*, 1933, **10**, 330). These measurements were repeated at least twice with two independent specimens of the original sol in each case, and in some, with two dilutions of the colloid

The change in transparency for white light by *thermoageing* was determined by means of a Duboscq colorimeter as described in a previous paper (Joshi and Kulkarni, *ibid.*, 1936, **13**, 441). Data in the 4th and 5th columns in Table I show respectively the heights in mm. of each of the sols before and after *thermoageing* matched for equal transparency.

TABLE I.

Influence of thermoageing on the viscosity and transparency.

Colloid content (g./litre).	Viscosity		Transparency		Remarks.
	Before	After.	Before.	After.	
As_2S_3 (3·05 g.)	1·012	1·006	56 mm.	50 mm.	
,, ,,	1·013	1·004	33	29	
MnO_2 (1·46 g.)	1·002	1·008	20	25·3	
,, ,,	1·003	1·009	15	19	
HgS (6·18 g.)	1·010	1·007 (5 mins.)	0·5	0·75	Coagulated in 1 hr, at about 97° ; thermo-aged for short periods as shown. Colour changes from dark brown to dark grey.
,, ,,	1·008	1·007 (0·5 hr.)	,,	,,	
Sb_2S_3 (1·6 g.)	1·003	1·002	35	38·1	

Table I (*contd.*).

Colloid content (g./litre).	Viscosity		Transparency		Remarks.
	Before.	After.	Before.	After.	
Sb_2S_3 (1·6g.)	1·004	1·002	35	38·1	
,, (0·89 g.)	1·003	1·001	65	67·5	
,, ,,	1·003	1·001	65	67·5	
Fe_2O_3 (2·0 g.)	1·023	1·016	30	27·5	
,, ,,	1·023	1·015	40	36·0	
,, ,,	1·023	1·015	45	40·0	
,, (1·0 g.)	1·014	1·010	35	30·0	
,, ,,	1·014	1·010	50	43·5	
,, ,,	1·014	1·009	60	52·2	
$Fe_4[Fe(CN)_6]_3$ (0·5 g.)	1·008	1·007	—	—	Colour changes from blue to green.
,, ,,	1·008	1·007	—	—	
MoO_3 (2·5 g.)	1·009	1·010	37	40	Colour changes sensibly from blue to violet blue.
,, ,,	1·008	1·009	46	50	
,, (1·25 g.)	1·006	1·007	50	55	
,, ,,	1·006	1·007	50	55	
Se (1·2 g.)	1·004	1·004	50	18	Viscosity and transparency measurements were made 3 hrs. after '*thermoageing.*' Longer treatment produced flocculation.
,, ,,	1·004	1·004	60	20	
V_2O_5 (3·2 g.)	1·020	1·042	9	6	The transparency of the normal sol is poor.
,, ,,	1·023	1·042	—	—	
,, (1·06 g.)	1·006	1·007	19	14	,, ,,
,, ,,	1·006	1·008	—	—	
Al_2O_3 (0·5 g.)	1·011	1·02	—	—	The sol was '*thermoaged*' for about 10 hrs.
,, ,,	1·010	1·019	—	—	
Linseed oil emulsion	1·024	1·016			Creaming is produced to a small extent on '*thermoageing.*'
,,	1·023	1·016			
Til oil emulsion	1·025	1·072			
,, ,,	1·025	1·072			

DISCUSSION.

It is known that a freshly prepared colloid attains to its equilibrium state slowly or otherwise, depending on the nature of the system, on simply allowing it to stand. This is the so-called '*ageing*'. During this period, there occur reactions (which are almost always irreversible), such as the hydrolysis of the dispersed material and the passage from the latter of the stabilising (or opposite) ions and molecules, into the continuous medium and outside. These affect the size of the particles and some of their characteristic constants such as the charge, the dielectric constant, the state of the micellar hydration, etc. These reactions are accelerated at the higher temperatures used in 'thermoageing'. Presumably, therefore, 'thermoageing' differs from ordinary ageing in degree and not so much in kind. The behaviour of colloidal HgS is interesting ; it shows that '*ageing*' and coagulation might be to an appreciable extent cognate, in origin and mechanism of reaction. The above colloid *autocoagulates* (that is, coagulates, without the introduction of an external material) simply by 'ageing' in about 10 days, or in a very much shorter period by 'thermoageing'. In this, the release of H_2S (or a similar stabilising material) would appear to be a reasonable factor. The extent to which such a factor would operate depends chiefly upon the nature of the colloid for example, colloid As_2S_3 can stand, *i.e.*, 'age' for long periods of time and thermoage' for at least 24 hours without appreciable instabilisation taking place, although the H_2S, which is known to be a stabiliser for the colloid, is expected to be released slowly or rapidly depending on the temperature to which the system is exposed.

It is interesting to note from the results in Table I that η, the viscosity is not altered always in the same sense as a result of '*thermoageing*'. In the majority of the cases studied, η decreases slightly on '*thermoageing*', in four cases out of nine it has increased. The case of colloidal selenium is peculiar in that '*thermoageing*' does not produce any sensible change in η. In this connection it is of interest to recall an earlier finding in these laboratories, *viz.*, that in numerous coagulations of colloid As_2S_3 (Joshi and Kulkarni, *loc. cit.*), and colloid Sb_2S_3 (Joshi and Menon, *ibid.*, 1937, **14**, 103) by *mercury chloride*, the viscosity of the coagulating system remained *stationary*. This shows that in so far as 'thermoageing' is analogous to coagulation, viscosity change [and on independent evidence (*loc. cit.*) even turbidity] is no *general* measure of the degree of the corresponding micellar change involved. The marked influence of the nature of the micellar material on η is shown by the result in Table I, that while 'thermoageing' leads to an increase of η in the case of Al_2O_3 sol, the opposite is observed with the apparently similar Fe_2O_3. It also follows that although simpler than coagulation, '*ageing*' is too complex a phenomenon to be measured by change of any single property. Results are available from the work of numerous investigators on changes by '*ageing*' in the adsorptive capacity, flocculation value, micellar change, double refraction, cataphoretic velocity, intensity of the Tyndall cone, conductivity and viscosity. These do not allow of any simple generalisation by reason of mutually exclusive findings, which change from colloid to colloid. The result obtained previously in these laboratories, that in 19 colloids '*thermoageing*' produces an increase of refractivity is interesting. In by far the majority of cases and in agreement with our results (for η) viscosity decreases and conductivity increases by '*ageing*'; the latter change is due to the release of ions from the particles into the solution phase.

It is interesting to consider the effect of '*thermoageing*' on the transparency as shown by Table I. This property seems to have increased in the majority of cases and might be due to a diminution of particle size, which is in agreement with the earlier finding of a general increase in refractivity, also attributed to the same origin. Usually though not invariably (Joshi and Kulkarni, *loc. cit.*; Joshi and Menon, *loc. cit.*, Joshi and Purushottam, *Current Science*, 1936, **4**, 870) coagulation decreases transparency; *the contrary* might, however be conceived if a simple coalescence leads to an increase in the free inter-particle space. It has been emphasised in previous communications (Joshi and co-workers, *J. Indian Chem. Soc.*, 1933, **10**, 329, 599; 1934, **11**, 133, 555, 573, 797; 1936, **13**, 309, 311; *J. chim. phys.*, 1935, **32**, 455; *Proc. Acad. Sci. U. P.*, 1935, **5**, 41.; *J. Bombay Univ.*, 1935, **4**, 140; *Fettchem. Umsch.*, 1936, **3**, 36; *Kolloid Z.*, 1936, **76**, 145) that both viscosity and transparency changes are inadmissible as a general measure of the corresponding degree of coagulation. The data in Table I support this deduction. Like coagulation, 'thermoageing' represents a certain micellar change. Subject to the above limitation, it is anticipated that increase of viscosity might be accompanied by a diminution of transparency, so familiar in coagulation phenomena. The above results for 'thermoageing' show, however, the inadequacy of such a generalisation. Thus for example, in the case of colloidal MnO_2, 'thermoageing' produces an increase both in viscosity and transparency; in Fe_2O_3 and As_2S_3 sols, both these quantities diminish, the former rather slightly. These results show that either 'ageing' and coagulation are almost entirely different, or what is more probable, viscosity and transparency do not necessarily increase and diminish respectively in a coagulation.

Work is in progress on the absorption spectra of a number of ' thermoaged ' sols. These results will be published shortly.

SUMMARY.

The changes of viscosity and transparency (for white light) consequent on ' thermoageing ' are studied for two oil emulsions and colloidal solutions of As_2S_3, Sb_2S_3, MnO_2, HgS, Fe_2O_3 and Prussian blue. The last two show change of colour Majority of others show a decrease in viscosity and increase in transparency. In some cases, decrease in transparency is accompanied by a like change in viscosity, and *vice versa*. It is suggested that these properties, *viz.*, viscosity and opacity do not *necessarily* increase during coagulation.

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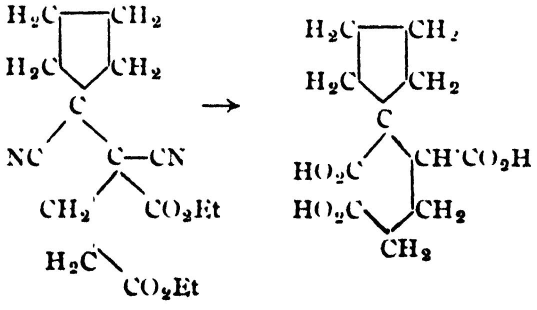
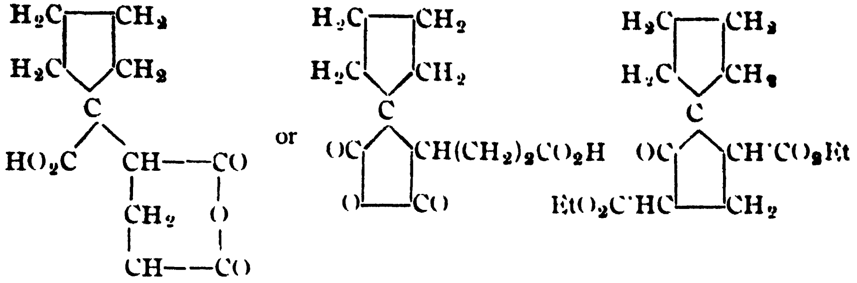
SPIRO-COMPOUNDS. PART IV FORMATION OF SPIRO-COMPOUNDS FROM *CYCLO*PENTANONE. SYNTHESIS OF *CYCLO*PENTANE-SPIRO-*CYCLO*PENTANE AND ITS DERIVATIVES.

By Nripendra Nath Chatterjee.

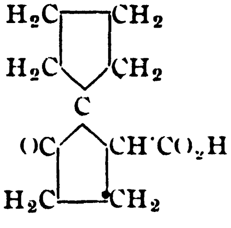
It follows from the model that *cyclo*pentane has got a coplaner structure, whereas the *cyclo*hexane ring is in a dynamic condition changing from one multiplaner form to another, thus passing through an intermediate stage when it is coplaner and consequently a strained one. Now assuming that the average condition of the vibrating framework is between the uniplaner and strainless conditions, the difference in the case of formation and stability of the analogous spiro-compounds built up with these two types of rings will be a measure of the difference in strain in them. With the hope of gaining some quantitative idea of the nature of strain in these rings, spiro-compounds with *cyclo*pentane ring have been built up by a method similar to that described in a previous communication (Chatterjee, *J. Indian Chem. Soc.*, 1936, **13**, 536). *cyclo*Pentanone cyanohydrin, obtained through its bisulphite compound, is allowed to react in alcoholic solution with the sodium salt of ethyl cyanoacetate. The sodio derivative of the condensation product, thus obtained, is treated with ethyl β-chloropropionate to yield diethyl 1-cyano*cyclo*pentane-1-α-cyanoglutarate (I). This cyano-ester on hydrolysis by means of sulphuric acid (70%) yields a mixture of *cyclo*-pentane-1-carboxylic-1-α-glutaric acid (II) and its acid anhydride (III). The pure acid is obtained by treating the above mixture with caustic alkali (15%). The corresponding ester undergoes ring-closure in presence of sodium giving diethyl *cyclo*pentane-spiro-*cyclo*pentane 2-one-3:5-dicarboxylate (IV). In alcoholic solution this ester gives a violet colouration with ferric chloride and when hydrolysed by means of sulphuric acid (20%) gives *cyclo*pentane-spiro-*cyclo*pentane-2-one-5-carboxylic acid (V). The constitution of this keto-acid is proved by its oxidation to *cyclo*pentane-1:1-dicarboxylic acid. This acid loses carbon dioxide when heated with the formation of *cyclo*pentane carboxylic acid. The product (V) showed all the properties of a keto-acid. By the Clemmensen reduction of the keto-acid (V) a product (VI) is obtained which failed to crystallise even on keeping for a long time in a vacuum desiccator over sulphuric acid. It showed no properties of a ketone, but when the calcium salt of this acid is heated with lime in vacuum *cyclo*pentane-spiro-*cyclo*-pentane (VII) is obtained in a very poor yield. This hydrocarbon slowly decolourises a solution of permanganate. The product (VI) is heated with selenium for a long time with the expectation that a ring transformation will take place, but no definite product could be isolated.



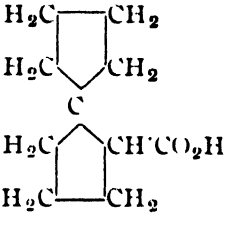
(I) (II)



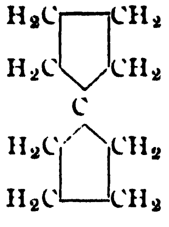
(III) (IV)



(V)



(VI)



(VII)

The fact that the yield of the spiro-compound (IV) is of the same order as that of the *cyclo*hexane analogue (*cf.* Chatterjee, *loc. cit.*) shows that the difference in strain in *cyclo*hexane and a *cyclo*pentane ring is not of a very high order.

In this connection it may be mentioned that there is a difference in stability among the spiro-hydrocarbons (*a*) *cyclo*hexane-spiro-*cyclo*hexane, (*b*) *cyclo*hexane-spiro-*cyclo*pentane and (*c*) *cyclo*pentane-spiro-*cyclo*pentane as regards the action of permanganate on them. Compound (*a*) does not decolourise a solution of permanganate (*cf* Norris, *J. Chem. Soc.*, 1926, 245), whereas (*b*) and (*c*) decolourise a solution of permanganate slowly. This suggests that in a spiro-hydrocarbon the presence of *cyclo*pentane ring makes it slightly unstable.

EXPERIMENTAL.

Diethyl 1-*cyanocyclopentane*-1-α-*cyanoglutarate* (I).—To a well cooled solution of freshly distilled *cyclo*pentanone-cyanohydrin (190 g.) in absolute alcohol (190 g.) a suspension of ethyl sodiocyanoacetate, obtained from ethyl cyanoacetate (168 g.), sodium (33 g.) and alcohol (500 c.c.) was gradually added with vigorous shaking. The mixture after being kept in ice for 6 hours and at room temperature for 3 days, was mixed with ethyl β-chloropropionate (240 g.) and after initial reaction had abated, boiled under reflux until a test portion diluted with water was netural to litmus (about 40 hours). The mixture was filtered and the filtrate diluted with water and extracted with ether, the ethereal extract washed with a large volume of water to remove most of the alcohol and dried. The ester distilled as a viscous liquid, b. p. 208°-215°/4mm., yield 150 g. (Found: C, 62·5; H, 7·0. $C_{16}H_{22}O_4N_2$ requires C, 62·7; H, 7·1 per cent).

1 *Carboxycyclopentane-1-α-glutaric Acid* (II).—The ester (20 g.) was mixed with 6 vols. of 70% sulphuric acid and boiled under reflux for 12 hours. The condenser was removed from the flask from time to time to allow the alcohol formed to escape. The solution was then diluted with water and extracted with ether and the acid thus obtained was freed from neutral matter by extraction with sodium carbonate. The resulting product is a mixture of the required tribasic acid and its acid anhydride and it was heated on a water-bath with a solution of caustic alkali (15%) for 3-4 hours. It was then acidified and repeatedly extracted with ether. After removing ether the product was kept in a vacuum desiccator when it solidified. It crystallised from ether, m.p. 131°-32. This acid when heated with zinc chloride and resorcin gives a compound which shows bluish fluorescence on addition of alkalis. It is not much soluble in ether, yield 12 g. (Found: C, 54·3; H, 6·5. $C_{11}H_{16}O_6$ requires C, 54·09; H, 6·5 per cent).

Triethyl cyclo*Pentane-1-carboxylate-1-α-glutarate* was obtained by esterifying the above acid in an almost quantitative yield by alcohol vapour method. In a typical experiment the acid (25 g.), absolute alcohol (80 c.c.), concentrated sulphuric acid (8 c.c.), 3 litres of vapourised alcohol (3 hours) gave 28 g. of the ester, b p. 162°-65°/4mm. (Found: C, 62·3; H, 8·4. $C_{17}H_{28}O_6$ requires C, 62·19; H, 8·5 per cent).

Diethyl cyclo*Pentane-spiro* cyclo*pentane-2-one* 3:5-*dicarboxylate* (IV).—A mixture of the foregoing ester (20 g.) and granulated sodium (2·3 g.) in dry benzene (50 c.c.) was refluxed for 10 minutes to start the reaction. The heating was discontinued until the vigour of the reaction abated and was then continued for 2 hours. After cooling the product was treated with cold dilute sulphuric acid and the benzene layer was washed with aqueous sodium carbonate and with water, dried, and evaporated. The residue in alcoholic solution gave a violet colouration with ferric chloride. The ester was obtained as a pale yellow oil (9 g.), b.p. 180°-85°/4 mm. (Found: C, 63·8; H, 7·7. $C_{15}H_{22}O_5$ requires C, 63·8; H, 7·8 per cent).

cyclo*Pentane-spiro*-cyclo*pentane-2-one-5-carboxylic Acid* (V)—The ester (IV) was refluxed with excess of dilute sulphuric acid (20%) for 12 hours and the cooled solution was saturated with ammonium sulphate and repeatedly extracted with ether and the extract washed with water and dried with anhydrous sodium sulphate. After removing the ether it was kept in a vacuum desiccator over sulphuric acid when it solidified in needle-shaped crystals, m.p. 67° after previous softening. (Found: C, 66·0; H, 7·6. $C_{10}H_{14}O_3$ requires C, 65·9 ; H, 7·6 per cent).

The *semicarbazone* crystallised from absolute alcohol, m.p. 232°. (Found: N, 17·5. $C_{11}H_{17}O_3N_3$ requires N, 17·5 per cent).

Ethyl cyclo*Pentane-spiro* cyclo*pentane-2-one-5-carboxylate* —The ester prepared by refluxing a solution of the keto-acid (10 g.) in absolute alcohol (40 c.c.) with absolute alcohol (5 c c.) saturated at 0° with hydrogen chloride, formed a colourless somewhat viscous oil (10 g.) b.p. 131°-32°/ 4 mm. (Found: C, 68·2; H, 8·4. $C_{12}H_{18}O_3$ requires C, 68·5; H, 8·5 per cent).

cyclo*Pentane-spiro*-cyclo*pentane* (VII).—The pure keto acid (10 g.), amalgamated zinc (35 g.), and concentrated hydrochloric acid (50 c.c) were refluxed for 12 hours, further acid (35 c.c.) was added and the heating continued for 12 hours. After extraction with ether a product was obtained which even on keeping for a long time in a vacuum desiccator over sulphuric acid did not solidify. This product showed no properties of a ketone but when the calcium salt was heated with lime *cyclo*pentane-spiro *cyclo*pentane was obtained in a very poor yield. The calcium salt and lime were well ground up together and heated in a distilling flask, the receiver being a test tube with a side-tube which was connected to the suction pump. The oil was fractionated several times, and a pure fraction of *cyclo*pentane-*spiro-cyclo*pentane was collected at 60°/12 mm. It slowly decolourises a solution of permanganate. (Found: C, 87·3; H, 12·6. C_9H_{16} requires C, 87·09 ; H, 12·9 per cent).

Oxidation of cyclo*Pentane-spiro*-cyclo*pentane*-2-one-5-*carboxylic Acid*.—The keto-acid (V) was warmed with an excess of concentrated nitric acid untill most of the red fumes disappeared. The resulting solution was then boiled for a few minutes and finally evaporated to dryness. The residue was treated with water and again evaporated. The semi-solid mass, thus obtained, was crystallised repeatedly from benzene, ether and light petroleum (b.p. 40-60°), m.p. 187° (lit. m.p. 187°). On distillation this acid gives *cyclo*pentane carboxylic acid.

My sincere thanks are due to Prof. P.C. Mitter for encouragement and advice during the course of this work.

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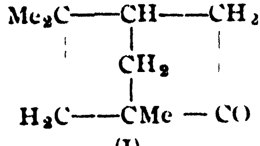
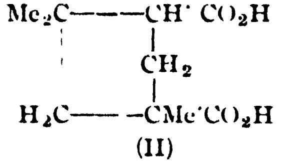
EXPERIMENTS TOWARDS THE SYNTHESIS OF *ISO*-FENCHONE. PART I. A SYNTHESIS OF βδ-DIMETHYLPENTANE-βδε-TRICARBOXYLIC ACID.*

By S. K. Ranganathan.

Bertraum and Helle (*J. pr Chem.*, 1900, *ii*, **61**, 293) found that the hydration of *l*-α-fenchene with sulphuric—acetic acid mixture gave rise to *iso*-fenchyl alcohol, different from fenchyl alcohol. On oxidation with chromic acid, the new alcohol yielded *iso*fenchone (I). The subsequent degradation experiments of Wallach (*Annalen*, 1907, **357**, 49; 1908, **363**, 1 ; 1909, **369**, 97) and more notably of Aschan (*Annalen*, 1912, **387**, 1) and Tiovonen (*ibid.*, 1919, **419**, 176) on the ketone brought to light a series of interesting compounds amongst which *iso*fenchocamphoric acid (II) and *iso*fenchocamphononic acid (III) may be mentioned. Although very careful degradation work has established the structures (I), (II) and (III), no synthetic evidence, however, has been adduced for any of them and the need for work in this direction becomes obvious. In the present paper is recorded the synthesis of βδ-dimethylpentane-βδε-tricarboxylic acid (VI, R = H). *iso*Fenchocamphononic acid (III) too was synthesised starting from (II) but in this the author has been anticipated by Bardhan and Ganguly (*J. Chem Soc*, 1936, 1852) and detailed description is, therefore, not made of this part of the work.


(I)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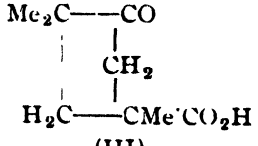
(III)

Ruzicka's method (*Ber.*, 1917, **50**, 1367) in his classical synthesis of fenchone was adopted for the present synthesis. Ethyl mesitonate (ethyl αα-dimethyllaevulate) (IV) (Pinner, *Ber.*, 1882, **15**, 579; *cf.* Anschutz and Gillet, *Annalen*, 1888, **287**, 99) condensed with zinc and ethyl bromoacetate to yield the lactone of ethyl β-hydroxy-βδδ-trimethyladipate (V). The lactonic ester added potassium cyanide at 220 , and hydrolysis of the nitrile and simultaneous esterification (*cf.* Ruzicka, *loc.cit.*) yielded ethyl βδ-dimethylpentane-βδε-tricarboxylate (VI, R = Et). The conversion of this to (III) was accomplished by cyclising it with sodium in benzene to (VII) and hydrolysing and decarboxylating the latter.

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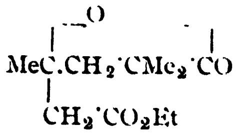
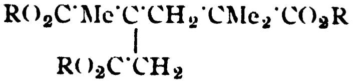
* A short preliminary note about this work appeared in *Current Science* (1936, **5**, 199).

$Me\cdot CO\cdot CH_2\cdot CMe_2\cdot CO_2Et$

(IV)

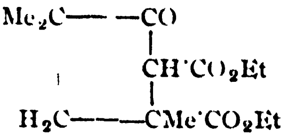


(V)



$RO_2C\cdot MeC\cdot CH_2\cdot CMe_2\cdot CO_2R$ with $RO_2C\cdot CH_2$

(VI, R = H, Et)



(VII)

Experiments are in progress towards the preparation of (III) in quantity with a view to utilising it for the synthesis of *iso*fenchone (I) and *iso*fenchocamphoric acid (II).

EXPERIMENTAL.

Mesitonic Acid.—Pinner's method (*Ber.*, 1881, **41**, 1072) was adopted. The process was tedious and the yield was poor (10-14 g. from 100 g. of acetone).

Ethyl Mesitonate (IV).—The following procedure gave a good yield of the substance. Mesitonic acid (69 g.) was mixed with absolute alcohol (100 c.c.) and sulphuric acid (1·5 c.c.) and alcohol vapour from boiling alcohol (460 c.c.) was bubbled through the mixture for 1½ hours. After cooling, water was added, the ester layer taken up in ether, the ethereal solution dried and ether removed. Ethyl mesitonate was collected at 108-10°/25mm. (112-115°/28mm.), yield 70 g.

The *Semicarbazone* separated from an aqueous alcoholic solution of semicarbazide hydrochloride, sodium acetate and the ester. It crystallised from dilute alcohol in colourless needles, m.p. 154°. It is soluble in commoner organic solvents and in boiling water. (Found : N, 18·63. $C_{10}H_{19}O_3N_3$ requires N, 18·36 per cent).

The 2:4-*Dinitrophenylhydrazone* was prepared following the details of Allen (*J. Amer. Chem. Soc.*, 1930, **52**, 2950). It crystallised from alcohol in which it was sparingly soluble in slender orange needles, m.p. 98°; easily soluble in acetone and chloroform. (Found: N, 16·13. $C_{15}H_{20}O_6N_4$ requires N, 15·92 per cent).

Lactone of Ethyl β-Hydroxy-βδδ-trimethyl adipate (V).—Ethyl mesitonate (64·5 g.) was dissolved in benzene (200 c.c.) and zinc wool ("Reformatsky," 25 g.) was added. Ethyl bromoacetate (30 g.) was then added and the mixture heated on the water-bath (½ hour) when the exothermic reaction started. The reaction was maintained by the gradual addition of the remaining bromo-ester (33 g.) and when the addition was over, the flask was heated on the water-bath for 1 hour more to complete the reaction. After cooling the contents were treated with ice-cold dilute sulphuric acid, the benzene layer separated, washed successively with dilute sulphuric acid, dilute ammonia and water, dried and benzene removed. The benzene residue yielded after repeated fractionation the lactonic ester as a thin, colourless liquid, b.p. 137-38°/6 mm. (122°/1-2 mm.), yield 30 g. A high boiling fraction, 180°/3-4 mm. was also obtained (*cf.* Ruzicka, *loc. cit.*). The lactonic ester was insoluble in dilute sodium carbonate solution but dissolved slowly in *N*/10- alkali. From the solution, the silver salt could be precipitated. (Found: C, 61·76; H, 8·83. $C_{11}H_{18}O_4$ requires C, 61·67; H, 8·41 per cent). d_{20}^{20}, 1·0648; $n_D^{28·8}$, 1·4430.

Lactone of β-Hydroxy-βδδ--trimethyladipic Acid.—The ester (5 g.) was boiled for 1 hour with caustic potash (4 g.) in alcohol (35 c.c., 80 %), the solution was evaporated after addition of water, the residue extracted with ether and then acidified with hydrochloric acid. The lactonic acid separated as an oil which solidified immediately. It was recrystallised from water in prisms, m.p. 128-29°. (Found: C, 57·7; H, 7·9. $C_9H_{14}O_4$ requires C, 58·0; H, 7·5 per cent).

Action of KCN *on the Lactonic Ester* : *ββ-Dimethylpentane-βδε-tricarboxylic Acid and its Ethyl ester* (VI).—The above lactonic ester (28 g.) was mixed with finely powdered potassium cyanide (12·8 g.) and the mixture heated under reflux on a paraffin-bath at 220° for 10 hours. The brownish black semi-solid mass was treated with concentrated hydrochloric acid (100 c.c.) and refluxed for 10 hours on an oil-bath. The product was evaporated cautiously and the residue exhaustively extracted with ether (12 times), the ethereal solution dried and the ether removed. The residue (18·2 g.) solidified in part. For obtaining the tricarboxylic acid, the crude product (2 g.) was dissolved in sodium carbonate solution and extracted with ether to remove any neutral impurities. Reacidification and extraction with ether and removal of ether gave a product which solidified partly. This was triturated with concentrated hydrochloric acid and filtered. The solid acid melted at 172°. *βδ-Dimethylpentane-βδε-tricarboxylic acid* (VI, R = H) melted after two recrystallisations from dilute hydrochloric acid (plates) at 185-86°, the m.p. not rising with further crystallisations. (Found : C, 51·75 ; H, 7·2. Equiv., 77·75. $C_{10}H_{16}O_6$ requires C, 51·72 ; H, 6·9 per cent. Equiv., 77·3).

The above method of hydrolysis was not satisfactory, very small yield of the tricarboxylic ester being obtained on esterifying the crude product. Some unreacted lactonic ester was recovered. Ruzicka's method (*loc. cit.*) was found to be better. To the crude product of reaction obtained from the lactonic ester (20 g.) and potassium cyanide (9·3 g.), absolute alcohol (65 c.c.) and sulphuric acid (35 g.) were added and the mixture heated for 9 days under gentle reflux on an oil-bath. The product obtained was poured into water and the oily layer extracted with ether, the ethereal solution dried and ether removed The brownish residue was distilled in vacuum when a main fraction, b.p. 165-170°/7-8 mm. (9.3 g.) was obtained. Redistillation yielded ethyl *βδ*-dimethylpentane-*βδε*-tricarboxylate (VI, R=Et) as a thick pale yellow oil, b.p. 153-155°/2 mm.; $n_D^{28\cdot8}$, 1·4525. (Found : C, 60·74; H, 8·74. $C_{16}H_{28}O_6$ requires C, 60·8; H, 8·86 per cent).

Cyclisation of VI (R=Et) *to* (VII).—The method and results are identical with those of Bardhan and Ganguly (*loc. cit*).

Hydrolysis and Decarboxylation of (VII) *to* (III).—Results are identical with those of Bardhan and Ganguly except for the figure for m.p. of the semicarbazone of *iso*fenchocamphononic acid. It (prisms from water) melted at 212-13° (decomp.) and at 218° in a bath previously heated to 210°. (Aschan gives 216-217° and 221° respectively).

The author's grateful thanks are due to Prof. P. C. Guha for his interest in the investigation. He is indebted to the Government of Madras for a scholarship.

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THE OIL FROM THE SEEDS OF *XIMENIA AMERICANA*, LINN. A NEW UNSATURATED FATTY ACID, XIMENIC ACID.

By S. V. Puntambekar and S. Krishna.

Ximenia americana, Linn. (Syn. *Ximenia Russelliana*, Wall), N. O. *Olacaceae*, Vern., *Kondanakkera* (Telugu), is a shrub found in abundance in the coastal tracks of Tennasserim, the Southern Maharatta country, Mysore and in many districts of the Madras Presidency. It bears fruit, an ovoid drupe of an orange red colour which when ripe has a pleasant taste. It is used for jam making. The kernels of the seeds taste like filberts and like almonds when roasted. In Southern India these are extracted for the oil which is used as a substitute for *Ghee* (Fischer, *Indian Forester*, 1918, **44**, 264).

Ximenia americana also occurs in South Africa and in South America and the oil from these sources has been examined mostly for its constants (Grimme, *Chem. Rev.*, 1910, **17**, 157; Schröder, *Arbb. d. Kaiserl. Gesundsh.*, 1911, **43**, 454; Freise, *Seifens Z.*, 1931, **58**, 131; *Bull. Imp. Inst.*, 1935, **33**, 277) but a complete chemical examination of this oil or the oil from the *Ximenia* seeds of Indian origin does not appear to have been made so far.

During the separation of the mixed acids of the oil into solid and liquid acids by Twitchell's method it was observed that the solid acids had too high an iodine value (33·9) to be attributed to the small amount of oleic acid which at times accompanies them. The possibility of the presence of an isomeric solid oleic acid (Puntambekar and Krishna, *J. Indian Chem. Soc.*, 1933, **10**, 209) was suggested but later ruled out as no dihydroxystearic acid was found among the products of oxidation of the solid acids with cold and dilute potassium permanganate. Instead, however, an oxy-acid very sparingly soluble in petroleum ether and of m.p. 118-19° (M. W. 425), was isolated in pure condition. This high molecular weight and the fact that the main component of the solid acids is cerotic acid made it appear that the oxy-acid might be a dihydroxy derivative of an unsaturated solid acid also of 26 carbon atoms accompanying cerotic acid ($C_{26}H_{52}O_2$). This inference was strengthened by the fact that its M. W. (425) and combustion data (C, 72·4%; H, 11·8%) closely agree with that of dihydoxycerotic acid, $C_{26}H_{52}O_4$ (M. W. 428; C, 72·8%; H, 12·2%). An additional proof that the unsaturated acid in the solid acids is a C_{26}-acid was supplied by catalytic hydrogenation of the crystallised acids, m. p. 61-62°, M. W. 400·5, iodine value 43·7, obtained from the fraction IV of the distilled solid ester when a product (m. p. 83-84°, M. W. 398·4, iodine value nil) was obtained and identified as cerotic acid. It is thus evident that this new unsaturated fatty acid belonging to the oleic acid series is a hexacosenic acid. Its separation in pure state, however, has not yet been possible because of its intimate combination with cerotic acid and hence our inability to present complete data on this new acid, which we hope will form the subject matter of a later publication. But at this stage we propose to designate it as ximenic acid.

EXPERIMENTAL.

The seeds of *X. americana* were obtained from Vizagapatam forest division of the Madras Presidency and consisted of :—air-dried pulp with shell 55%; cream coloured soft kernels 45%; moisture in kernel 3·6%; oil in kernel 49·0%

For determination of its physical and chemical constants, the oil was expressed from the kernels at 50 in a hydraulic press. It was very viscous and mucilaginous and the quantity small and therefore for further examination it was extracted from the seeds with petroleum ether. The latter oil was pale yellow and of not unpleasant odour or taste.

Physical and Chemical Constants.

The Fatty Oil.

	The authors.	Earlier workers.
Country of origin :	South India.	South and East Africa ; South America.
Specific gravity at 20	0·9262	0·9165 0·9248 at 15°
Refractive index at 20°	1·4710	1·4737
Iodine value (Hanus)	82·5	80·9—94·5
Saponification value	169·2	155·3—183·1
Acid value	2·3	1—24·6
Hehner value	—	93·9—94·8
Reichert-Meisel value	Nil	—
Unsaponifiable matter	1·7	0·5—2·9

Mixed Acids.

	The authors.	Earlier workers
Mean molecular weight	319·8	322·6—326
Iodine value	85·0	71—100·1
Saturated acids	31·0%	—
Unsaturated acids	67·5%	—
Resin acids	1·5%	—

Composition of the Fatty Acids.

500 G. of the oil were saponified in the usual manner with alcoholic sodium hydroxide. On distilling off the alcohol and dissolving the resultant soap in water a large amount of rubbery mass, apparently a portion of the unsaponifiable matter, separated out. It was filtered off and then the remaining portion of the unsaponifiable matter in the mixed acids was removed by the usual procedure.

200 G. of the mixed acid, free from the unsaponifiable matter, were separated into solid and liquid acids by performing the Twitchell's operation twice and the separated acids had the following constants.

Acids.	Iodine value.	Mean M. W.	Net weight.
(S) Solid	33·9	381·5	62·0 g.
(L) Liquid	99·2	322·5	135·0
Resin	—	—	3·0

Solid Acids (S).

A small portion of the solid acids after three crystallisations from alcohol melted at 83-84°, M. W. 398·3. Further crystallisations did not change these constants indicating thereby the crystalline product to be one homogeneous substance, probably cerotic acid.

The high iodine value of the solid acids indicated their association with some unsaturated acids, very likely with some solid unsaturated acid

(Puntambekar and Krishna, *loc. cit.*). In order to identify this acid 5 g. of the solid acids were oxidised in cold alkaline solution with dilute aqueous permanganate according to the modified method of Hazura (Lewkowitsch, "Chemical Technology and Analysis of Oils, Fats and Waxes", Vol. I, 6th Ed., p. 575). The oxidised product after being extracted with petroleum ether in a soxhlet to remove the unoxidised acids and some of the acids of decomposition, was twice crystallised from 95% alcohol, m p. 118-19°. (Found : C, 72·4 ; H, 11·8; M. W., 425. $C_{26}H_{52}O_4$ requires C, 72·8 ; H, 12·2 per cent. M. W. 428·4). It appears to be dihydroxy-cerotic acid. It thus appears that the unsaturated acid occurring in the solid acids is a hexacosenic acid, a C_{26}-acid belonging to the oleic series

Of the remaining portion of the solid acids 50 g. were converted into methyl esters by methyl alcoholic hydrochloric acid. After refluxing the mixture for 5 hours and cooling to room temperature, a solid crystalline product (16·3 g.) separated out. It was washed with fresh methyl alcohol and crystallised from acetone, giving a product looking like mother of pearl and melting at 63-64°. The acid liberated from this ester had an iodine value of 1·7 and after three crystallisations from alcohol melted at 83 84°, M. W. 400·5. This appears to be cerotic acid isolated above from solid acids by direct crystallisation, and was confirmed as such by its unchanged mixed melting point with the former acid.

The mother liquor and the washings of the above ester, methyl cerotate (m.p. 63-64°), were combined together and the methyl alcohol was distilled off. The residual esters were taken up in ether, washed with 5% sodium carbonate to remove the unesterified acids and then with water. The ethereal solution was dried and the ether distilled off. The esters (31·5 g.) were then fractionated at 3 mm. into the following fractions.

Fractions.	B p.	Wt.	Iodine value	M. W of the acids.	Component of methyl esters.		
					Stearate.	Ximenate.	Cerotate.
S_1	180-190°	0·75 g	13·7	287·6	0·58 g.	0·17 g	–
S_2	190 200°	1·40	18·6		0·98	0·42	—
S_3	200-220°	1·70	32·4	341·0	0·82	0·88	—
S_4	220-270°	16·45	47·9	394·7	—	12·65	3·80 g.
Residue	—	11·00	49·1	—	—	8·67	2·33
Loss	—	0·20	—	—	—	—	—
	Total	31·50			2·38	22·79	6·13

Fractions S_1 and S_2 being similar and small in quantity were mixed together and saponified. The resulting mixed acids melted at 48-49°, M. W. 287·6. On crystallisation from dilute alcohol a product, (m.p. 57-58°, M. W. 314·6) was obtained. The acids from mother liquor had a M. W. 282. The amount of material at this stage being too small further fractional study was not possible but from the iodine value of the fractions and of the M. W. of the liberated acids it appears that they mostly consist of stearic and ximenic acids. The presence of the latter acid in total solid acids has already been described above. The presence of a small amount of oleic acid in these fractions, however, is not ruled out but to simplify the calculations the iodine value is assumed to be due to ximenic acid only.

The acids from fraction S_3 had M. W. 341. When crystallised from acetone they gave a product melting at 60-61°, M. W. 381 and a residue with a M. W. of 290. Again in this case the M W. of the residual acids and the iodine value of the ester fraction suggests that they consist of stearic and ximenic acids. The presence of the cerotic acid is ruled out on the consideration that ximenic acid, as shown by the iodine value, forms a little over 50% of the fraction, the remaining 50% must be made of an acid of lower molecular weight (stearic acid) so as to make the M. W. of the total acids of the fraction 341.

The acids liberated from fraction S_4 had M. W. 394·7. These when crystallised from alcohol gave a product melting at 61-62°, M. W., 400·4 ; iodine value, 43·7. On hydrogenation of this product (2·5 g. in alcohol) for an hour and half in presence of platinum oxide catalyst (according to Adams), a crystalline product melting at 83-84°, M. W. 398·4 and iodine value nil, was obtained and found to be cerotic acid isolated above. The fraction is, therefore, a mixture of ximenic acid ($C_{26}H_{50}O_2$) and cerotic acid ($C_{26}H_{52}O_2$).

The acids liberated from the residual esters were extracted with petroleum ether (60—80°) to remove them from oxidised or resinified matter. After the petroleum ether was driven off on a water-bath and then under vacuum, the extracted acids had a mean M. W. of 417 and iodine value 46·7 and were presumably a mixture of ximenic and cerotic acids. The somewhat high mean molecular weight of the acids is probably due to the fact that the products of oxidation or polymerisation have not been completely removed by petroleum ether.

Liquid Acids (L)

These were saponified to break up any ethyl ester which might have been formed during the Twitchell separation. The iodine value (99·2) of the resulting acids indicates them to be a mixture of unsaturated acids consisting of two and more double bonds.

A portion of the liquid acids was converted into potassium soaps and oxidised in cold by a dilute solution of potassium permanganate according to the modified method of Hazura (*loc. cit.*). From the oxidised product only dihydroxystearic acid (m.p. 130-31°, M. W. 316) could be isolated and identified. When, however, it was boiled with a large volume of water and the mixture quickly filtered a small amount of a white crystalline material (m.p. 155-58°) presumably one of the or a mixture of isomeric tetrahydroxystearic acid separated out. No hexahydroxystearic acid was found in the aqueous filtrate from the products of oxidation. The unsaturated acids in the liquid acids, therefore, appear to consist of mainly oleic and a small amount of linoleic acids.

Another portion of the liquid acids was converted into methyl esters and 103 g. of them were separated into the following fractions by distillation under 6 mm.

Fraction.	B.p.	Iodine value.	Wt.
L_1	165°	59·3	2·44
L_2	165-85°	76·5	2·19
L_3	185-95°	86·8	23·63
L_4	195-97°	94·4	25·37
L_5	107-203°	98·2	8·15
L_6	203-10°	100·3	4·97
L_7	210-30°	86·7	6·74
Residue	—		26·67
Loss	—		2·84
		Total	103·00

Fractions L_1 and L_2 and L_4, L_5, L_6 and L_7 being similar were mixed together. Portions of these mixtures and of L_3 were separately saponified and then oxidised with dilute permanganate in the cold. In the product of oxidation from the first mixture and from L_3 only dihydroxystearic acid could be isolated and identified, whereas both dihydroxy and tetrahydroxystearic acids were found in the oxidised acids from the second mixture. The residue was a very dark viscous mass containing mostly the methyl oleate and methyl linoleate together with all the colouring matter of the mixed acids.

The above results of the fractional distillation of the methyl esters of the solid and liquid acids on calculation gave the following percentage composition for the fatty acids :—

Stearic (not isolated in pure form), 1·2%; cerotic, 15·2%; ximenic, 14·6% ; oleic, 60·8 ; linoleic, 6·7%; resin, 1·5%.

Unsaponifiable Matter.

The rubber like product separated from the soap solution after saponification of the oil constituted most of the saponifiable matter. Being insoluble in most of the organic solvents and in dilute mineral acids and alkalis it was not worked up further. The small amount of unsaponifiable matter, isolated from the sodium soaps of the mixed acids in the usual way by extraction with ether, showed the presence of a phytosterol (precipitate with a solution of digitonin in alcohol) but the amount was very small for its identification.

SUMMARY.

The oil from the seeds of *Ximenia americana*, Linn. consists of the glycerides of stearic, cerotic, ximenic, (hexacosenic), oleic and linoleic acids together with a small amount of a phytosterol and a large amount of a rubber like substance. Arachidic acid reported by Schröder (*loc. cit.*) was not found.

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A NOTE ON RAMAN SCATTERING OF SILICATE SOLUTIONS.

By S. K. Chakravarti and P. B. Ganguli.

A large number of sodium silicates containing different proportions of silica can be obtained. Starting with the meta-silicate where the ratio between $Na_2O : SiO_2$ is as 1 : 1, one can easily prepare solutions of increasing silica content even up to the ratio 1 : 4. In view of the large variation in the proportion of silica which is possible, the question of fixing the molecular nature of these solutions becomes a complicated one. The question is further complicated by the hydrolysis undergone by the silicate solutions. The extent of hydrolysis was studied by Kohlrausch (*Z. physikal. Chem.*, 1893, **12**, 773) from measurements of electrical conductivity and by Kahlenberg (*J. Phys. Chem.*, 1898, **2**, 77), and Lumis (*Annalen*, 1897, **60**, 531) from freezing point lowering measurements. They found that the alkali silicates were largely hydrolysed in aqueous solutions giving rise to an amount of free silica which tended to pass into the colloidal state. Bogue (*J. Amer. Chem. Soc.*, 1920, **42**, 2575), however, showed that the degree of hydrolysis as determined by E. M. F. measurements was unexpectedly low and was at variance with the conclusions drawn from conductivity and other measurements.

The sodium silicates have been exhaustively studied by Harman (*J. Phys. Chem.*, 1928, **32**, 44). He concludes that the solutions with the ratio 1 : 1 and 1 : 2 only contain definite salts namely Na_2SiO_3 and $NaHSiO_3$. Above the ratio 1 : 2, as the proportion of silica increases colloidal silica is in evidence. In concentrated solutions of the higher ratios, a larger colloidal aggregate containing both sodium and silica has been found.

In previous papers by one of us (*J. Phys. Chem.*, 1926, **30**, 706), it has been inferred that the silicate solutions contain colloidal micelles and that the amount of the colloid increases rapidly after the ratio 1 : 3 is exceeded.

Although in the literature many references to sodium silicates like Na_2SiO_3, $Na_2Si_2O_5$, $NaHSiO_3$, Na_2SiO_{11}, Na_4SiO_4 etc., exist the only sodium silicate whose molecular composition is definitely known is the meta-silicate. In the present paper, therefore, the Raman scattering of the meta-silicate as well as that of the higher ratio solutions have been investigated. For the purposes of comparison the scattering of a dialysed solution of silicic acid has also been studied. If the higher ratio sodium silicate solutions be allied in molecular nature to the sodium meta-silicate, all these solutions might give a common Raman shift characteristic of the common ingredient between them all. If on the other hand the higher ratio silicate solutions contain an appreciable amount of fine grained colloidal silica, they might behave with respect to Raman scattering in a manner analogous to that of a dialysed solution of silicic acid. As will be seen in the following pages, the same Raman shift, as is obtained with the meta-silicate solution, is also obtained with the higher ratio silicate solutions, but with increase in the proportion of silicate in these solutions there is a large amount of general or Rayleigh scattering which takes away the sharpness of the Raman bands. This behaviour is expected if the higher ratio silicate solutions are to contain increasing amounts of colloidal matter.

EXPERIMENTAL.

The following solutions were investigated :

1. Solution of sodium meta-silicate. (2) Solution of sodium silicate containing Na_2O : SiO_2 in the ratio 1 : 2. (3) Solution of sodium silicate of ratio 1 : 4 (4) Dialysed solution of silicic acid.

The last named solution was prepared by Graham's method. The concentration of the solution was 10% with respect to its silica content. The other solutions were carefully analysed and were made equivalent such that all the solutions contained the same amount of silica, *viz.*, 24·88 g. per 100 g. of the solution. All the solutions were protected from atmospheric carbon dioxide.

The exciting source used was the mercury arc, the ultra-violet portion being cut off by the interposition of a glass plate. The tube containing the solution was placed at the focal plane of an ellipsoidal vessel and was kept cool by circulating a stream of water. To get a good reflecting surface, the interior of the vessel was plated and polished.

The exciting line in each case was taken to be the 4358 mercury line. Microphotographic prints were taken from the plates some of which are reproduced in the accompanying diagram. In the case of the Na_2SiO_3 and the 1 : 2 ratio solution, fairly sharp peaks corresponding to the modified lines were obtained, but in the case of the other two solutions sharpness was absent. To locate the position of the modified lines a somewhat magnified microphotograph was taken. Figures 2—5 refer to these magnified microphotographs of the meta-silicate, of the 1 : 2 ratio solution, of

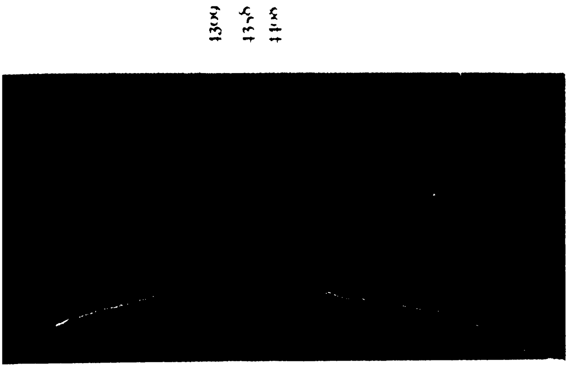

FIG. 1

Sodium meta silicate

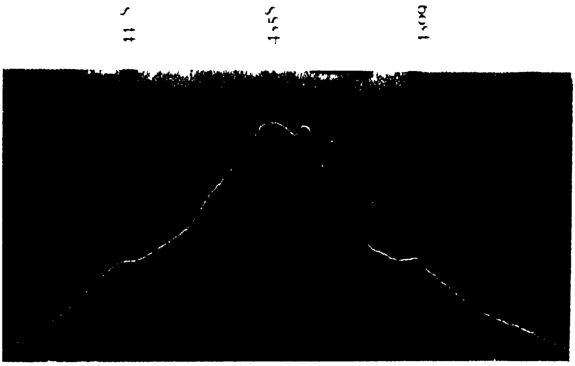

FIG. 2

Sodium meta silicate

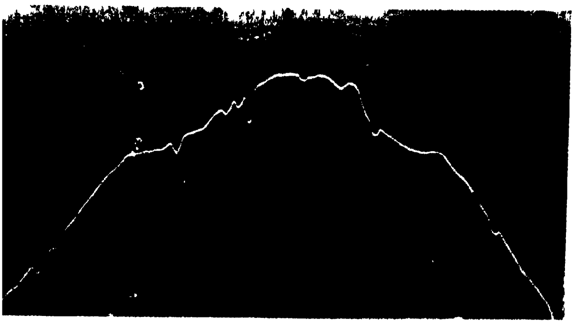

FIG. 3

1 : 2 ratio silicate soln

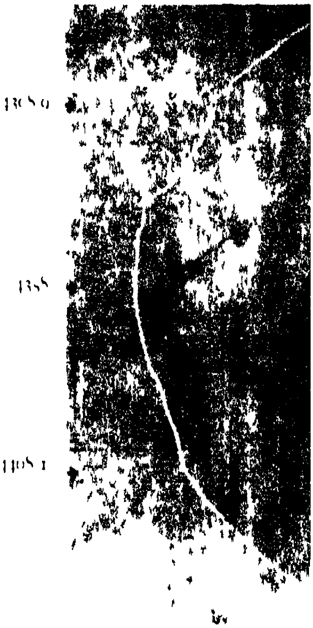

FIG. 4.

1 : 4-ratio silicate soln.

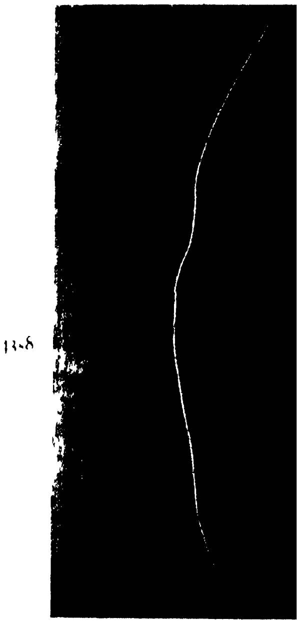

FIG. 5.

Colloidal silicic acid

the 1 : 4 ratio solution and of the dialysed silicic acid solution respectively. The values are given in the following table.

	Solution.	Exciting line.		Modified line.		$\Delta\nu$.	λ.
		λ.	ν	λ.	ν_1		
				4309	23208A.S.	261	38·3μ
1	Na_2SiO_3	4358	22947	4408	22686	261	38·3
				4309·4	23206	259	38·6
2	1 :2 Solution	4358	22947	4407·7	22687	260	38 5
				4308·9	23209	262	38·2
3	1 :4 ,,	4358	22947	4408·1	22685	262	38·2
				4309·2	23207	260	38 5
4	Colloidal silicic acid	4358	22947	4407·6	22688	259	38·6

Sodium meta-silicate gives a Raman shift equal to $\Delta\nu = 261$ cm^{-1} and exactly the same modified line is given by the two higher ratio silicate solutions. It is evident, therefore, that there is some constituent which is common to all these solutions. It is interesting to recall that the shift as obtained in the present experiments corresponds to one of the modified lines for quartz obtained by Krishnan (*Nature*, 1928, **122**, 477) and also by Czenny (*Z. Physik*, 1929, **53**, 317). Probably this shift is due to SiO_2 group which is present in all these systems. Although the plate obtained with 1 : 2 and 1 : 4 silicate solutions give the same modified lines, they differ to a very marked extent so far as the sharpness of the bands is concerned. In the case of the 1 : 4 ratio solution, there was pronounced general scattering similar to that obtained with the dialysed silicic acid sol. So far as these experiments go, it seems reasonable to infer that collodal matter increases quite rapidly.

The measurement of the photographic density of the plates at a fixed distance from the exciting lines for the various solutions is likely to yield some interesting information about the colloidal content of the higher ratio solutions. Further work on the above lines is in progress.

In conclusion we wish to express our thanks to Professor Kamta Prosad for his kind interest in the work and to Mr. B. N. Ghosh for help with the microphotometer.

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PEROXIDASES. PART IV. A METHOD OF ESTIMATING PEROXIDASE ACTIVITY FROM E. M. F. MEASUREMENTS

By M. V. Sitharaman and S Rengachari.

It has been shown in a previous paper (Dey, Rengachari and Sitharaman, *J. Indian Chem. Soc.*, 1936, **13**, 390) that potentiometric titrations can be successfully applied for estimating the peroxidase activity of plant saps when hydroquinone is employed as the substrate and the advantages of the method have been referred to therein. Since hydroquinone and its oxidation product, quinone, form a reversible oxidation-reduction system, it was hoped that potential measurements might be employed to find out the unreacted hydroquinone in the peroxidase reaction mixture thus leading to a comparison of the relative merits of the two methods of estimating peroxidase activity.

Haber and Russ (*Z. physikal. Chem.*, 1904, **47**, 257) have shown that the reversible reduction of quinone to hydroquinone could be considered from the electrochemical standpoint and that the Van't Hoff reaction isotherm was applicable, the reaction being similar in character to oxidation and reduction reactions in the case of electrolytes. The reaction taking place is represented by the equation

$$\underset{\text{(Hydroquinone)}}{C_6H_4(OH)_2} \rightleftharpoons \underset{\text{(Quinone)}}{C_6H_4O_2} + 2H^+ + 2\ominus$$

Their method lay in finding out whether the observed differences in potential of two solutions containing different ratios of hydroquinone-quinone measured separately against a calomel electrode, agreed with the theoretical values calculated from the Van't Hoff expression, keeping the acidity of the solution constant.

These results have been confirmed by Granger and Nelson (*J. Amer. Chem. Soc.*, 1921, **43**, 1401), who took into account the actual concentrations of the reactants, the acidity of the solutions which was varied, and the degree of dissociation of quinhydrone, which they always found out when quinone and hydroquinone were present in solution instead of assuming as Haber and Russ (*loc cit.*) had done, that the quinhydrone was completely dissociated.

Stern and Day (*J. Biol. Chem.*, 1929, **85**, 299) have employed the change in potential that occurs when air is bubbled through a solution of quinhydrone, properly bufferred, as a means of detecting certain sufficiently active oxidases or oxygenases, choosing potato oxidase as the most suitable. They have found that the potential rise initially observed under conditions stated above is restored partially by adding further quantities of quinhydrone and that the observed potentials compared reasonably with the potentials calculated on the basis of the Van't Hoff equation.

The potential of an inert electrode, *e.g.*, platinum or gold, immersed in a solution containing quinone and hydroquinone is usually given by the expression,

$$\pi = \pi_0 + \frac{RT}{2F}\ ln\ \frac{C_Q\, C_H^2}{C_{H_2Q}} = \pi_0 + \frac{RT}{2F}\ ln\ \frac{C_Q}{C_{H_2Q}} + \frac{RT}{F}\ ln\ C_H.$$

This oxidation-reduction potential of the quinone-hydroquinone system, involving as it does a feebly ionised or practically unionised organic compound, is dependent on the hydrogen-ion activity of the solution. If, therefore, the reference electrode and the hydrogen-ion concentration of the system be kept constant, the E.M.F. of the system will alter with the ratio of the quinone to hydroquinone. If π be the potential of the quinhydrone electrode, π_1 that of the reference electrode (here 0·1*N* calomel), then since the quinhydrone electrode is more positive than calomel, the observed E.M.F.

$$E = \pi - \pi_1 = \pi_0 + \frac{RT}{F}\ ln C_H + \frac{RT}{2F}\ ln\ \frac{C_Q}{C_{H_2Q}} - \pi_1$$

$$= \left[\pi_0 + \frac{RT}{F}\ ln\ C_H - \pi_1\right] + \frac{RT}{2F}\ ln\ \frac{C_Q}{C_{H_2Q}}$$

since π_0, π_1 and the hydrogen-ion concentrations are kept constant.

$\therefore\ E = E_0 + \frac{RT}{2F}\ ln\ \frac{C_Q}{C_{H_2Q}}$, where E_0 is the expression within brackets. If conditions are so chosen that E_0 is constant, then the above expression can be used to compare the E.M.F. of the system as regards observed values for different ratios of quinone to hydroquinone. The expression when $t = 0°$ becomes,

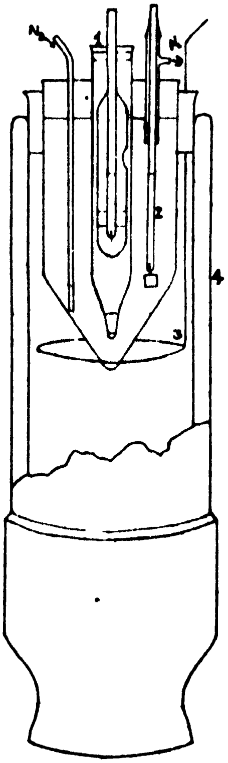
$$E = E_0 + 0{\cdot}0271\ \log \frac{C_Q}{C_{H_2Q}} = E_0 - 0{\cdot}0271\ \log \frac{C_{H_2Q}}{C_Q}$$

In the peroxidase reaction the initial condition is represented by the system comprising of (*i*) the volume of buffer solution added, (*ii*) volume of sap added, (*iii*) volume of hydroquinone solution, and (*iv*) the volume of hydrogen peroxide, the temperature of the reactants and the temperature of the mixture being the same. After a certain interval of time (generally 18 minutes) the reaction is stopped by the addition of hydrochloric acid. The condition then is represented by (*i*) the volume of the buffer, (*ii*) the volume of the sap, (*iii*) the volume of hydroquinone left over, (*iv*) the volume of hydrogen peroxide left over, (*v*) the quinhydrone in solution, neglecting the precipitated amount, and (*vi*) the volume of hydrochloric acid added for inhibiting the reaction. If the amount of unreacted hydroquinone is to be determined by potential measurements, a study must be made of the variations of the E.M.F. of a solution, with respect to the variations in concentration of hydroquinone, all other conditions enumerated above remaining constant. The concentration of hydroquinone in any other solution which is identical in the matter of every condition can be obtained directly from a hydroquinone concentration—E. M. F. curve. It was this method that was followed in the present investigation.

EXPERIMENTAL.

Experiments were conducted with the same saps that were employed or the previous investigation (*loc. cit.*) and it was found necessary to submit these saps to longer periods of dialysis (4 to 5 days) to eliminate electrolytes completely. Since temperature is an important factor in potential measurements and the activity of the saps is appreciable at temperatures considerably lower than the room temperature (30°-32°), it was considered best to carry out these experiments at 0° using a mixture of ice-water and ice in a good silvered wide-mouthed Dewar vessel, the bath being stirred mechanically for avoiding fluctuations of temperature. It was found in trials that the temperature remained constant for periods of 2 to 3 hours. The Dewar vessel was fitted with a bung which carried a Beckmann outer tube, 2″ diameter, drawn out to a conical shape at its closed end (*cf.* Fig. 1). This formed the reaction vessel and was closed by a three-holed rubber cork carrying (1) a dip-type calomel electrode (which was designed and made for the purpose since the available dip-type electrodes were of an inconvenient size (*vide* Fig. 1); (2) a platinum foil electrode (Hildebrand type) with an outlet for leading away gas ; and (3) a delivery tube for bubbling purified nitrogen gas, partly to keep an inert atmosphere within, since hydroquinone undergoes slow oxidation in air and partly to secure a good stirring of the reaction mixture. The nitrogen was obtained from a cylinder and was purified by passing through alkaline pyrogallol, concentrated sulphuric acid,

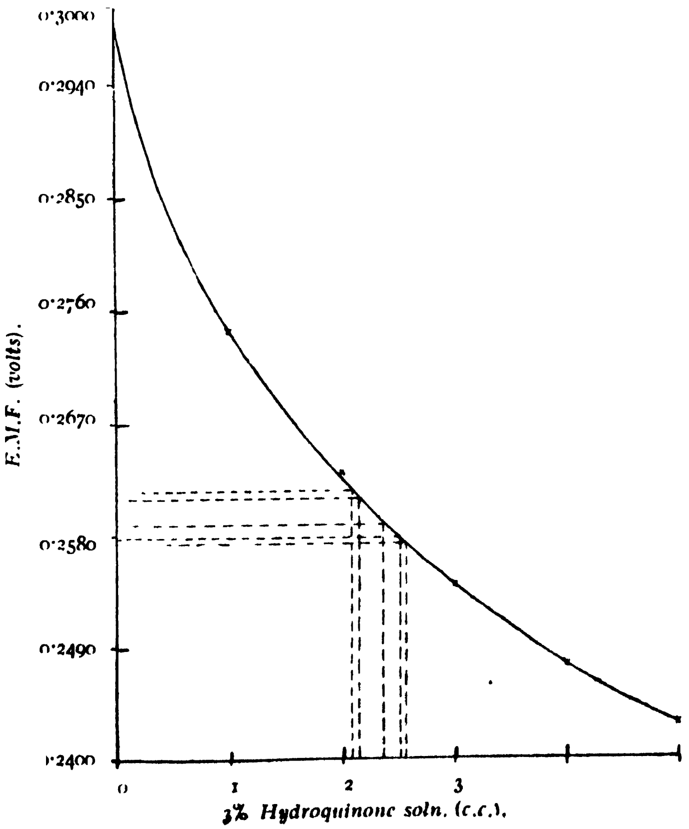
FIG. 1.



1-Dip type cal. electrode. 2-Pt foil electrode. 3-Stirrer. 4-Dewar flask.

water (conductivity) and finally through fused calcium chloride for drying. Conductivity water was used to prepare all solutions which were preserved in Jena glass bottles. Solutions of hydroquinone (exactly, 3·0%) were freshly prepared before use and preserved in dark amber-coloured bottles. The solutions were delivered from automatic microburettes. For potential measurements, a Leeds and Northrup **K**-type potentiometer and a portable sensitive mirror galvanometer were used, the voltage readings being accurate to 0·00005 volt. No correction for salt or protein error was applied though quinhydrone was used. The volume was adjusted to a final volume of 20 *c.c. of the reaction mixture*, which was maintained constant throughout the series of experiments. A buffer of sodium acetate and hydrochloric acid of p_H 4·58 was used. A decinormal calomel electrode (in the dip-type electrode vessel prepared) was used as the reference electrode in view of its temperature coefficient being very low compared with the other calomel

FIG. 2.



electrodes. In all cases sufficient quinhydrone was added to keep the solution saturated with respect to it.

The first stage in the series was to find by trial an indicator or reference solution which will be applicable to all saps, and possessing a constant and reproducible E.M.F. in the absence of hydroquinone. When hydroquinone is added, the E.M.F. gradually diminishes with increase of concentration of the hydroquinone. A reference to Table I (*a*), (*b*) will show that when mixtures were made up with 7 c.c. of the buffer (p_H 4·58), 2 c.c. of 2*N* hydrochloric acid, and 11 c.c. of water to make up to the constant volume of 20 c.c., the same initial E.M.F. of 0·2980 volt nearly, was reached. In Table I (*c*), where hydrogen peroxide (1 c.c. of 1% solution) was added with a corresponding reduction of water, the E.M.F. was unaffected. When increasing quantities of a 3·0% solution of hydroquinone (from 1 c.c. to 5 c.c. were added) the same potentials were registered in all cases (within experimental errors). It took nearly 45 minutes the equilibrium to reach and this interval of time was allowed to elapse in each case before final measurements were taken.

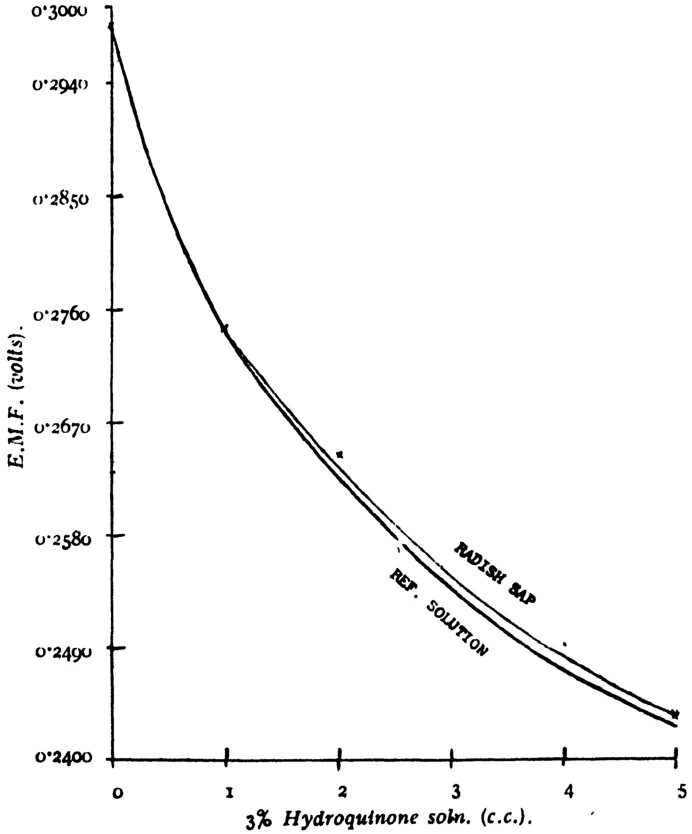
The hydroquinone concentration-E.M.F. relationship of the reference solution is given by the curve in Fig. 2, which was plotted by taking the averages of the three sets of experiments in Table I.

A repetition of the experiments with the three saps separately was made as shown in Tables II, III and IV. 5 C.c. of the sap were added in each case replacing the same volume of water, the total volume of 20 c. c. being maintained. The potentials are found to be in agreement with those in Table I (without the sap under the same conditions). Reference to Tables II (*c*), III (*c*) and IV (*c*) will show that the presence of hydrogen peroxide does not cause any alteration in the potentials, and that the reaction has been completely inhibited by the HCl added. From the measurements it is evident that $E_0 = 0{\cdot}2980$ volt with $C_Q/C_{H_2Q} = 1$, *i.e.*, $\log C_Q/C_{H_2Q} = 0$.

The change of potential with the alteration in the volume of the hydroquinone solution in the experiments with the different saps are plotted in Figures 3, 4 and 5.

The next stage was to study the peroxidase activity as usual with the three saps and estimate the hydroquinone left over by measuring the final potential of the system and comparing with the potentials of the reference solution. 7 C.c. of the buffer (p_H 4·58), 5 c.c. of 3·0% hydroquinone solution and 1 c.c. of 1% hydrogen peroxide were mixed in the reaction vessel cooled to 0°; 5 c c. of the sap at 0° were added while a current of nitrogen was bubbling through the solution. The reaction was allowed to proceed for 15 minutes at the end of which exactly 2 c.c. of 2·0*N* hydrochloric acid were quickly added from a microburette, the rate of bubbling of nitrogen being increased to effect a thorough mixing of the reaction mixture so that the reaction might be inhibited quickly. The nitrogen was kept bubbling for 45 minutes continuously at a slower rate at the end of which the E.M.F. was measured. From the E.M.F.—hydroquinone concentration curve of the reference solution, the concentration of the hydroquinone corresponding to the final E.M.F. observed in the test solution was obtained. This represents the hydroquinone (y) remaining in

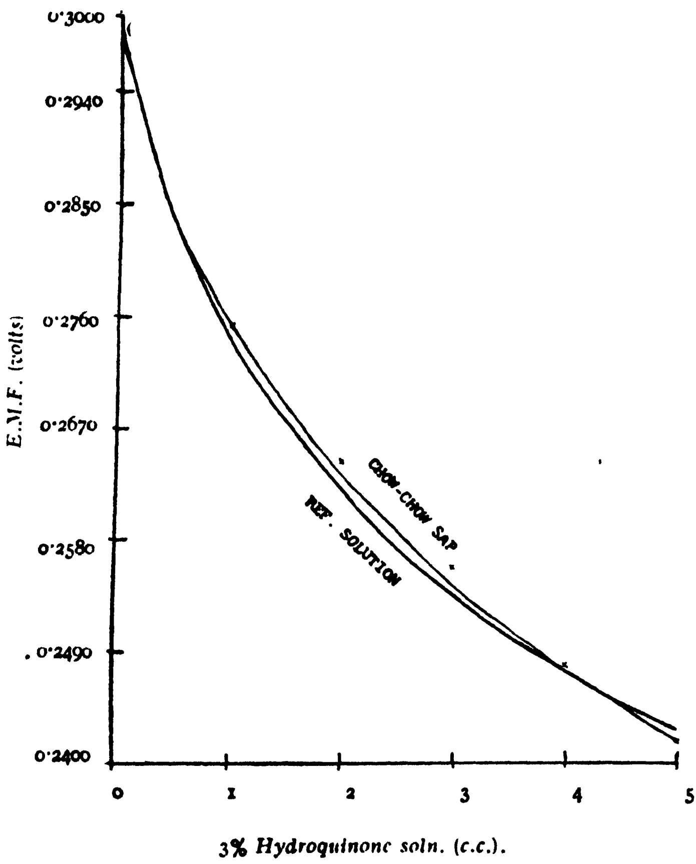
FIG. 3.



solution ; part of the unoxidised hydroquinone combining with the quinone formed to form the quinhydrone which was precipitated on account of its low solubility. Since the amount of hydroquinone taken (x) is known (being equal to 0·15 g. in all cases) and y, the amount of it left in solution is found out by experiment, the amount oxidised is $\frac{x-y}{2}$ corresponding to the quinone part of the quinhydrone formed.

The accuracy was also checked by diluting the reaction mixture to 100 c.c. as usual (*vide* the potentiometric method) and estimating the hydroquinone by potentiometric titration against standard potassium dichromate, the necessary blank experiments to find the intake of the

FIG. 4.



dichromate by the sap being duly performed. The results obtained in both the cases are found to agree well (*vide* Tables V, VI and VII).

The E.M.F. observed was then compared with the E.M.F. calculated theoretically on the following basis from the formula,

$$E = E_0 - 0{\cdot}0271 \log \frac{C_{H_2Q}}{C_Q} .$$

The concentration of the quinone is precisely the concentration obtained by the dissociation of quinhydrone, the solution being saturated with respect to it in all cases, since a precipitation of quinhydrone took place.

This concentration of quinone can be calculated from the solubility of quinhydrone in a solution identical in concentration of the reactants in the reaction mixture at the end of the reaction. 50 C.c. of a solution containing 6·25 c.c. of 3·0% hydroquinone, 17·50 c.c. of buffer (p_H 4·58), 5 c.c. of 2·0*N*-hydrochloric acid the rest being water was made up, excess of quinhydrone added and the mixture was agitated for two hours at 0° in a bath similar to the one used for the previous experiments. The solution was filtered by suction through cotton wool into another vessel kept in a similar bath at 0 . A definite volume of the solution was pipetted and the total hydroquinone in it determined potentiometrically by titration against standard potassium dichromate. The value for hydroquinone thus obtained is the sum of the hydroquinone initially taken together with the hydroquinone due to the solution of the quinhydrone, the latter being assumed, for the purpose of this investigation to be completely dissociated. By deducting the hydroquinone initially taken, from the total amount of hydroquinone, the hydroquinone part of the quinhydrone dissolved is obtained. The quinone part is equivalent to the hydroquinone thus determined. As a mean of three experiments, the value obtained was 0·03264 g. calculated as quinhydrone in 100 c.c. of the solution , so that in the reaction mixture of 20 c.c., the concentration of quinhydrone is 0·006528 g. which corresponds to 0·003233 g. of quinone and 0·003295 g. of hydroquinone. Now,

$$E = E_0 - 0{\cdot}0271 \log \frac{C_{H_2Q}}{C_Q}$$

E_0 being 0·2980 volt.

Calculating the potential of the system in Experiment I, Table VII, the amount of hydroquinone left over in solution (from the titration) is 0·0714 g. And since the quinhydrone dissolves to a certain extent and is assumed to have dissociated completely thus increasing the hydroquinone concentration

the amount of hydroquinone (H.Q.) present in solution $=0\cdot0714+0\cdot003295$
$=0\cdot0747$ g.

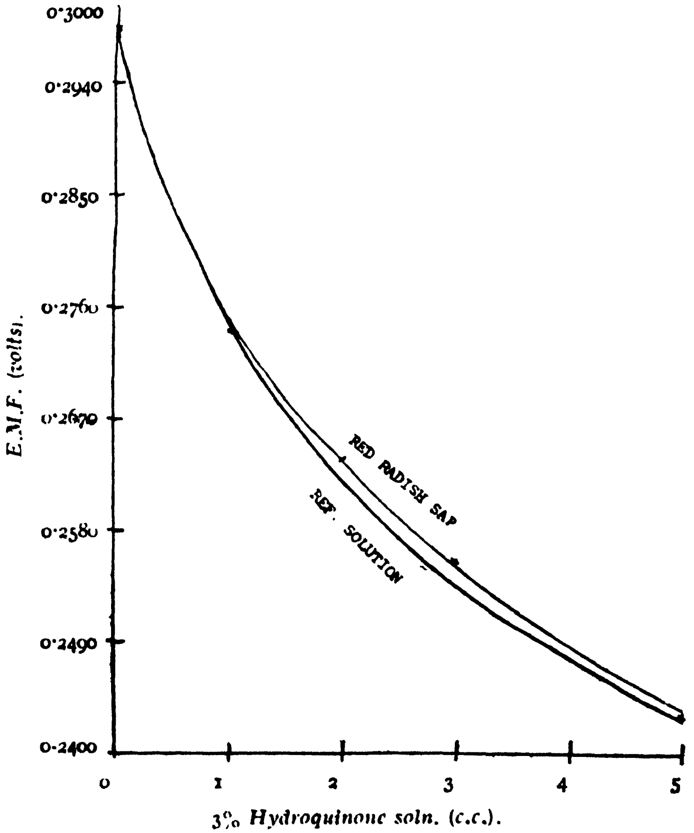
Amount of quinone (Q) in solution $=0\cdot003233$ g.

$$E=0\cdot2980-0\cdot0271\log\frac{0\cdot0747}{0\cdot003233}=0\cdot2610 \text{ volt (calculated).}$$

$E=0\cdot2590$ volt (observed).

The error is, therefore, less than 1%. Similar calculations in all the other cases give similar agreement between the calculated and the observed potentials.

FIG. 5.



Alteration of the E.M.F. with change in Hydroquinone Concentration in the reference Solution.

TABLE I.

Total volume in all cases = 20 c.c. buffer of p_H 4·58 added = 7 c.c. 2*N*-HCl added = 2 c.c.

	(a)		(b)		(c)	
					$1\%\ H_2O_2 = 1$ c.c.	
Vol. of 3·0% H.Q.	Vol. of water.	E. M. F. (volts).	Vol. of water.	E. M. F. (volts).	Vol. of water.	E. M. F. (volts).
Nil	11 c.c.	0·2980	11 c.c.	0·2982	10 c.c.	0·2980
1 c.c.	10	0·2745	10	0·2740	9	0·2740
2	9	0·2625	9	0·2628	8	0·2630
3	8	0·2545	8	0·2540	7	0·2540
4	7	0·2478	7	0·2473	6	0·2475
5	6	0·2425	6	0·2428	5	0·2427

TABLE II.

Experiments similar to those in Table I, the solutions containing 5 c.c. of dialysed radish (*Raphanus Sativus*) sap. Buffer of p_H 4·58 = 7 c.c. 2*N*-HCl added = 2 c.c.

	(a)		(b)		(c)	
					$1\%\ H_2O_2 = 1$ c.c.	
Vol. of 3·0% H.Q.	Vol. of water.	E. M. F. (volts).	Vol. of water.	E. M. F. (volts).	Vol. of water.	E. M. F. (volts).
Nil	6 c.c.	0·2990	6 c.c.	0·2980	5 c.c.	0·2985
1 c.c.	5	0·2735	5	0·2745	4	0·2745
2	4	0·2660	4	0·2635	3	0·2635
3	3	0·2555	3	0·2550	2	0·2560
4	2	0·2495	2	0·2490	1	0·2490
5	1	0·2440	1	0·2430	Nil	0·2435

TABLE III.

Experiments similar to those in Table I, the solutions containing 5 c.c. of dialysed chow-chow (*Sechium Edule*) sap. Buffer of p_H 4·58 added = 7 c.c. 2*N*-HCl taken = 2 c.c.

	(a)		(b)		(c)	
					1% H_2O_2 = 1 c.c.	
Vol. of 3·0% H_2O_2.	Vol. of water.	E. M. F. (volts).	Vol. of water	E. M. F. (volts).	Vol. of water.	E. M. F (volts).
Nil	6 c.c	0·2980	6 c.c.	0·2975	5 c.c.	0·2975
1 c.c	5	0·2755	5	0·2755	4	0·2740
2	4	0·2645	4	0·2647	3	0·2635
3	3	0·2560	3	0·2563	2	0·2550
4	2	0·2483	2	0·2485	1	0·2465
5	1	0·2415	1	0·2420	Nil	0·2415

TABLE IV.

Experiments similar to those in Table I, the solutions containing 5 c.c. of dialysed red radish sap (*Raphanus Sativus*, red variety). Buffer of p_H 4·58 = 7 c.c. 2N-HCl = 2 c.c.

	(a)		(b)		(c)	
					1% H_2O_2 = 1 c.c.	
Vol. of 3·0% H_2O_2.	Vol. of water.	E. M. F (volts).	Vol. of water.	E. M. F. (volts).	Vol. of water.	E. M. F. (volts).
Nil	6 c.c.	0·2985	6 c.c	0·2980	5 c.c.	0·2980
1 c.c	5	0·2735	5	0·2745	4	0·2735
2	4	0·2635	4	0·2640	3	0·2635
3	3	0·2560	3	0·2550	2	0·2555
4	2	0·2485	2	0·2485	1	0·2490
5	1	0·2430	1	0·2430	Nil	0·2430

Table V.

Reactions caried out with dialysed radish (*Raphanus Sativus*) sap, as described on p. 282, E.M.F. measured and results checked by titration.

	Expt. I.	Expt. II.
E. M. F. measured at the final stage	0·25785 volt.	0·2575 volt.
E. M. F. calculated from formula	0·2606 volt.	0·2608 volt.
H.Q. left in solution (*y*) obtained from the E. M. F.—H.Q. conc. curve of the ref. soln.	0·0745 g.	0·0771 g.
∴ Amount of H.Q. oxidised	0·0378 g.	0·0365 g.
Amount of H.Q. corresp. to $K_2Cr_2O_7$ titration.	*0·1119 g.	† 0·1137 g.
∵ Amount of H.Q. oxidised	0·0381 g.	0·0363 g.
Amount of H.Q. left as such in solution	0·0738 g.	0·0774 g.

* Being equivalent to 18·90 c.c. of 0·1076 N-$K_2Cr_2O_7$.

† Being equivalent to 19·20 c.c. of 0·1076 N-$K_2Cr_2O_7$.

Table VI.

Reaction carried out with dialysed chow-chow (*Sechium Edule*) sap, as described on p. 282, E.M.F. measured and results checked by titrations.

	Expt. I.	Expt. II.
E. M. F. measured at the final stage	0·2610 volt.	0·2615 volt.
E. M. F. calc. from formula	0·2622 volt.	0·2627 volt.
H.Q. left in solution (*y*), obtained from the E. M. F.—H.Q. conc. curve of the ref. soln.	0·0645 g.	0·0624 g.
∴ Amount of H.Q. oxidised	0·0428 g.	0·0438 g.
Amount of H.Q. corresp. to the $K_2Cr_2O_7$ titration.	* 0·1072 g.	† 0·1059 g.
∴ Amount of H.Q. oxidised	0·0428 g.	0·0441 g.
Amount of H.Q. left as such in soln.	0·0644 g.	0·0618 g.

* Being equivalent to 18·10 c.c. of 0·1076 N-$K_2Cr_2O_7$.

† Being equivalent to 17·90 c.c. of 0·1076 N-$K_2Cr_2O_7$.

TABLE VII.

Reactions carried out with dialysed red radish (*Raphanus Sativus*, red variety) sap as described on p. 282. E.M.F. measured and results checked by titrations.

	EXPT. I.	EXPT. II.
E. M. F. measured at the final stage	0·2590 volt.	0·2590 volt.
E. M. F. calc from formula	0·2610 volt.	0·2610 volt.
Amount of H_2Q left in soln (y), obtained from the E. M. F.–H_2Q conc curve of the ref. soln.	0·0708 g.	0·0708 g.
∴ Amount of H_2Q oxidised	0·0396 g.	0·0396 g.
Amount of H_2Q. corresp to the $K_2Cr_2O_7$ titration.	* 0·1107 g.	† 0·1107 g.
∴ Amount of H_2Q oxidised	0·0393 g.	0·0396 g.
Amount of H_2Q. left as such in soln	0·0714 g.	0·0714 g.

* Being equivalent to 18·70 c.c. of 0·1076 N-$K_2Cr_2O_7$.

† Being equivalent to 18·70 c.c. of 0·1076 N-$K_2Cr_2O_7$.

SUMMARY.

Since the hydroquinone and quinone (quinhydrone) form a reversible oxidation-reduction system, for which the Van't Hoff formula has been shown to be applicable, by keeping all factors except the ratio of H_2Q/Q constant, the amount of unreacted hydroquinone (substrate) can be estimated with reasonable accuracy by potential measurements. In this case the hydrogen peroxide left over does not affect the results or introduce any error and therefore need not be destroyed. All that is necessary is to make up a reference solution whose changes in potential have been previously studied for different ratios of hydroquinone to quinone, the concentration of the latter being that obtained by saturation of the solution with respect to quinhydrone. The results obtained show that a greater accuracy is possible with this method.

The authors wish to express their grateful thanks to Prof. B. B. Dey for his kind interest and valuable suggestions throughout the investigation.

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OXIDATION OF PHENOLS BY MEANS OF HYDROGEN PEROXIDE IN PRESENCE OF INORGANIC CATALYSTS.

By B. C. Kar.

The oxidation of phenols by means of oxygen and hydrogen peroxide has been carried out by many investigators in presence of oxidases, peroxidases and inorganic catalysts. Recently hydroquinone has been oxidised to quinhydrone in presence of peroxidase obtained from common Indian vegetables—"Jhinga" (*Luffa acutangula*) and "Chow chow" (*Sechium edule*) by Dey and Sitharaman (*J. Indian Chem. Soc.*, 1931, **8**, 479; 1932, **9**, 499). It has also been oxidised by peroxidase obtained from the fruits of "Linn" (*Tribulus terrestris*) by Ghatak and Giri (*Bull. Acad. Sci. U. P.*, 1933, **2**, 163). Jules Wolff (*Compt. rend.*, 1908, **146**, 781, 1217; **147**, 747) has shown the similarity in behaviour of certain iron salts and peroxidases by oxidising hydroquinone and pyrogallol in presence of hydrogen peroxide. When a colloidal ferrous ferrocyanide solution containing 10 mg. of iron per litre is added to a saturated solution of quinol, quinhydrone is formed in a minute or two. This artificial peroxidase resembles the natural peroxidases in certain respects. Its activity is destroyed by excess of hydrogen peroxide like the natural enzymes. It loses its activity on boiling. It can be filtered through paper without alteration but it becomes inactive when filtered through collodion. Similar oxidations by means of atmospheric oxygen and hydrogen peroxide in presence of different metallic salts such as manganese, copper, uranium have been carried out. The author has undertaken this work with the object of studying the analogy of the colloidal catalysts of tungstic acid, molybdic acid and vanadic acid with peroxidases and throwing some light on the mechanism of the enzymatic reactions. For this purpose, a representative selection of substances is taken and their behaviour towards the colloidal catalysts and peroxidases studied.

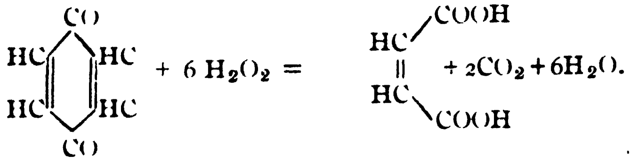
A. Oxidation of Hydroquinone by means of Hydrogen Peroxide in Presence of Tungstic Acid Sol.

The oxidation of hydroquinone by means of hydrogen peroxide occurs in a consecutive manner. At low concentrations of hydrogen peroxide and sol, quinhydrone is the main product of oxidation as is the case with peroxidases. But as the concentrations of sol and hydrogen peroxide are increased, it is converted into carbon dioxide and maleic acid. The equations may be expressed as follows.

(I). $2C_6H_4(OH)_2 + H_2O_2 = C_6H_4O_2{\cdot}C_6H_4(OH)_2 + 2H_2O.$

(II). $C_6H_4O_2{\cdot}C_6H_4(OH)_2 + H_2O_2 = 2C_6H_4O_2 + 2H_2O.$

(III).



Maleic acid

Kempf (*Ber.*, 1906, **39**, 3715) has oxidised quinone and hydroquinone by means of silver peroxide, sodium persulphate and ammonium persulphate and obtained carbon dioxide and maleic acid as the main products of oxidation, and formic acid and carbon monoxide are also produced in traces. The identical products of oxidation from hydroquinone by persulphates, and tungstic acid sol and hydrogen peroxide also support the formation of per-acids.

Isolation of the Products of Reaction.

Quinhydrone.—Quinhydrone can be easily isolated from the reaction mixture by starting with high concentrations of hydroquinone and adding equivalent amount of hydrogen peroxide in small quantities at a time, allowing a few minutes to elapse before each addition and cooling the reaction mixture in ice. Hydroquinone (2·5 g.) was dissolved in 150 c.c. of redistilled water and filtered. 0·05 M-sodium tungstate (5c.c.) in the form of sol was added and then equivalent amount of hydrogen peroxide. After the addition of hydrogen peroxide was complete, the reaction mixture was cooled in ice. The precipitated quinhydrone was filtered off, washed with ice-cold water and dried in a vacuum desiccator over sulphuric acid for a period of 72 hours. By this means a very pure quinhydrone was obtained having a sharp melting point of 171°, yield 0·4g.

Maleic Acid.—Hydroquinone (2 g.) was dissolved in redistilled water (100 c.c.) and filtered. Merck's perhydrol (35 c.c.) and 0·05M-sodium tungstate (100 c.c.) were then added. After a few minutes, the reaction began with the evolution of heat and carbon dioxide. The reaction mixture was then allowed to stand for about two weeks with occasional shaking. When the reaction was complete, the mixture having a slight yellow colour, was shaken with animal charcoal and excess of hydrogen peroxide was completely decomposed. It was then filtered and the filtrate did not liberate any iodine from a solution of potassium iodide in sulphuric acid. It was found to be distinctly acidic; it easily reduced potassium permanganate and decolourised bromine water. After evaporating the solution to dryness in a vacuum desiccator over sulphuric acid, maleic acid was extracted with ether.

Attempts were made to isolate any other products such as formic acid, oxalic acid and tartaric acid but were not successful.

Carbon dioxide. The formation of carbon dioxide can be easily shown by the method already given in the oxidation of cystine.

Measurement of Kinetics.

A sample of hydroquinone of chemically pure grade was taken and dissolved in water. In all our experiments we used redistilled water. Merck's perhydrol was taken for preparing fresh solution of hydrogen peroxide. The sol was prepared by the usual method.

In measuring the activity of peroxidase by oxidising hydroquinone to quinhydrone, Dey and Sitharaman (*loc. cit.*) separated the precipitated quinhydrone formed in a definite interval of time by filtration through Allihn tube. The quinhydrone was then dissolved in a mixture of alcohol and hydrochloric acid (1: 1) and a solution of KI was added. The liberated iodine was then estimated by thiosulphate. A correction for the loss of quinhydrone was made by carrying out a blank with known amount of quinhydrone but without hydrogen peroxide under identical conditions.

The author has found that instead of isolating the quinhydrone formed form the reaction mixture, which involves a certain amount of unavoidable error, it can be estimated in the reaction mixture itself spectrophotometrically by means of a Konig-Marten spectrophotometer. The reaction mixture after preparation was introduced into a small cell. It was then kept in a thermostat at a temperature of $(30 \pm 0{\cdot}1^\circ)$. After the reaction period (usually 45 minutes) the spectrophotometric reading was taken at a wavelength $525\mu\mu$ and $\log \tan \theta_1 / \tan \theta$ found out, where θ is the zero-reading usually 45° on the circular scale of the spectrophotometer and θ_1 is the reading after the time interval. The thickness of the solution was 8 mm. In this region of the spectrum, Beer's law is obeyed as shown, by Fig. 1, where the values of $\log \tan \theta_1 / \tan \theta$ plotted against concentration of quinhydrone give a straight line. Quinhydrone was prepared by adding hydrogen peroxide of moderate strength drop by drop in a mixture of sol and concentrated hydroquinone and cooling the mixture in ice as described before. A standard solution was prepared by dissolving it in a minimum quantity of hot water and roughly adjusted to the p_H of the reaction mixtures. All the experiments were repeated and concordant results were obtained. The results are expressed in terms of velocity constant

$$K = \frac{\log \tan \theta_1 - \log \tan \theta}{d.\,t.}$$

where d = the thickness of the solution expressed in mm., t = time in minutes, and are tabulated below.

TABLE I.

Quinhydrone (M)	...	0·0035	0·007	0·0105	0·014	0·0175
$\log \frac{\tan \theta_1}{\tan \theta}$	...	0·1001	0·1985	0·2991	0·3931	0·5056

TABLE II.

Effect of varying the concentration of hydroquinone.

Temp. = 30°. p_H = 3·2. H_2O_2 = 0·0238M. Sodium tungstate = 0·001M.

H.Q. (M)	...	0·00875	0·0175	0·02625	0·035	0·0525	0·07
K	...	0·00019	0·00034	0·00053	0·00072	0·000109	0·0014

TABLE III.

Effect of varying the concentration of H_2O_2.

Temp. = 30°. p_H = 3·2. H.Q. = 0·035M. Na-tungstate = 0·001M.

Conc. of H_2O_2 (M)	.	0·0238	0·0476	0·0714	0·0953	0·1191	0·1429
K	...	0·00072	0·00086	0·00094	0·001	0·00103	0·00103

TABLE IV.

Effect of varying the concentration of catalyst.

Temp. = 30°. p_H = 3·2. H.Q. = 0·035M. H_2O_2 = 0·0159M.

Conc. of Na_2WO_4 (M)	...	0·00025	0·0005	0·001	0·002
K	...	0·00019	0·00034	0·0007	0·00122

FIG. 1.

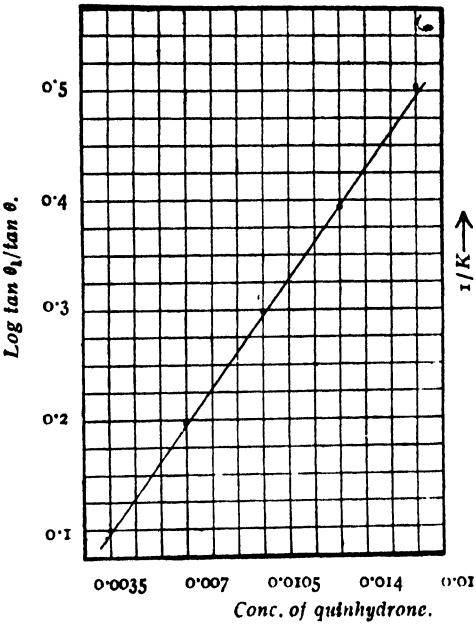


FIG. 2.

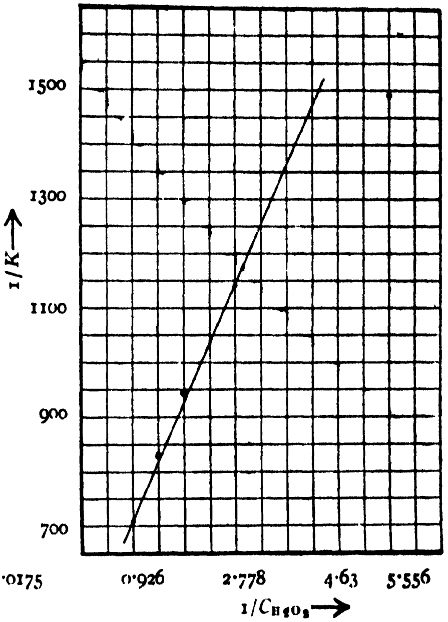


TABLE V.

Effect of varying the p_H.

Temp. = 30°. H.Q. = 0·035M. H_2O_2 = 0·0238M. Na-tungstate = 0·001M.

p_H ...	2·8	3·2	4·2	**The reaction is very rapid, gradually increasing with p_H.**
K	0·0006	0·00072	0·0013	

TABLE VI.

Temperature coefficient.

p_H = 3·2. H_2O_2 = 0·0238M. Na-tungstate = 0·001M.

	H.Q. = 0·035M			H.Q. = 0·07M	
Temp. ...	20°	30°	Temp ...	20°	30°
K ...	0·00024	0·00072	K ...	0.00045	0·0014

TABLE VII.

Effect of salts.

Temp. $=30°$. $p_H=3·2$. H.Q. $=0·035M$. $H_2O_2=0·0238M$.

Salts.	Conc. in the reaction mixture.	Conc. of sodium tungstate.	K
—	—	$10^{-3}M$	0.00072
$HgCl_2$	$10^{-3}M$	,,	0·00072
KCN	,,	,,	0·00072

In order to measure the kinetics of reaction (III), that is, oxidation of quinone into carbon dioxide and maleic acid, we used higher concentrations of sol and hydrogen peroxide. With high concentrations of sol and hydrogen peroxide the velocities of the reactions (I) and (II) become very rapid in comparison with the reaction (III).

We have always used hydrogen peroxide in excess and have measured the kinetics of the reaction by observing the pressure of carbon dioxide developed, as indicated by a mercury manometer, at any moment at constant volume. It is found that a very good unimolecular constant is obtained by applying the equation

$$K=\frac{1}{t_2-t_1}\log\frac{P\infty-Pt_1}{P\infty-Pt_2}$$

where Pt_1 is the pressure in cm. of mercury at any time t_1 (in minutes) and Pt is the pressure at time t_2 and $P\infty$ is the pressure that should theoretically develop in accordance with the equation given, $P\infty$ is obtained by means of the well known equation given in p. 298. An actual calculation how $P\infty$ is obtained is given in Table I (*vide infra*). $P\infty$ may also be obtained with excess of H_2O_2 by noting the difference of initial and final reading after 72 hours, of the mercury manometer at the same temperature. The theoretical and experimental values are almost equal if proper allowance is made of the decomposition of hydrogen peroxide after 72 hours, CO_2 being absorbed by caustic potash, and the change in the barometric pressure.

Owing to initial disturbance due to the first reactions, the velocity was measured from 8-10% to 50-55%.

The experiments were carried out in a constant volume type of respirometer (commonly called the Warburg type of manometer). The increase of pressure due to the production of carbon dioxide was indicated by a manometer filled with mercury. The total volume upto the constant mercury level in the manometer was 45·2 c.c. and was determined by filling the vessel and the tube with mercury. The reaction mixture occupied 10 c.c. and the rest 35·2 c.c. was the amount of dead space. No carbon dioxide was formed by the action of hydrogen peroxide on hydroquinone in the absence of the sol. The whole system was shaken 60 to 65 times per minute throughout the experiment. The vessels were completely immersed in a big thermostat which was maintained at a temperature of 25 ± 0·1°. To correct for the changes of temperature and the barometric pressure, a similar vessel which contained only water was used. It was always observed by keeping strict control in which the carbon dioxide was absorbed by caustic potash, in a suitable reservoir, that there was very slight spontaneous decomposition of hydrogen peroxide during the course of the experiment. All the experiments were repeated and reproducible results were obtained. In Table VIII is given the results of a typical experiment in detail.

TABLE VIII.

Temp.=25°. p_H =1·26. H_2O_2=0·72*M*. Na-tungstate=0·01*M*. H.Q.= 0·025 *M*. Composition of the mixture=2 c.c. water+2 c.c. H.Q.+2 c.c. dilute HCl+2 c.c. H_2O_2+2 c.c. sol.

Time.	Manometric readings. A.	Manometric readings. B.	Diff.	K.
0 min.	12	12	—	—
17	12	12·55	0·55 (1)	—
57	12	14·75	2·75 (2)	0·00122 (1&2)
94	12	16·6	4·6 (3)	0.00122 (1&3)
132·5	12	18·25	6·25 (4)	0·0012 (1&4)
169	12	19·7	7·7 (5)	0·0012 (1&5)
217·5	12	21·2	9·2 (6)	0·00116 (1&6)
P∞	—	—	21·4	
				Mean 0.0012

Calculation of P∞.—The amount of CO_2 that should theoretically generate in the above reaction mixture according to the equations given is 22 mg. and the volume it should occupy at N. T. P.

$$= \frac{22}{0{\cdot}089 \times 22}\ \text{c.c} = 11{\cdot}236\ \text{c.c.} = 11236\ \text{c. mm.},$$

0·089 mg. being the weight of 1 c.c. hydrogen at N. T. P. and 22 being the density of CO_2. Now the equation is

$$X = h\,\frac{{}^{*}\,V_G\,\frac{273}{T} + V_F\,\alpha}{P_0}$$

where x = the amount of gas evolved in c. mm. at N.T.P. = 11236 c. mm.,

h = corresponding reading of the manometer = P_∞ ?

V_G = the volume of the gas space in the vessel = 35200 c.mm.

T = absolute temperature of the water-bath = $(273+25)^\circ = 298^\circ$

V_F = the volume of the liquid in the vessel = 10000 c. mm.

α = the solubility of CO_2 in the liquid of the vessel at N. T. P. = 0·759 (*cf.* Bohr, *Ann. phys. Chem.*, 1899, **68**, 504).

P_0 = the normal pressure = 760 mm. Hg.

$$h = \frac{11236 \times 760\ \text{mm.}}{35200\,\frac{273}{298} + 10000 \times 0{\cdot}759} = 214\ \text{mm.} = 21{\cdot}4\ \text{cm.}$$

TABLE IX.

Effect of varying the concentration of hydroquinone.

Temp. = 25°. p_H = 1·26. H_2O_2 = 0·72*M*. Na-tungstate = 0·01*M*.

H.Q. (*M*) ...	0·0083	0·0125	0·0166	0·025	0·033
K (mean) ...	0·00125	0·00121	0·0012	0·0012	0·00118

---

[*] Here we have assumed the whole apparatus at temperature *T*. The manometric tube was, however, at room temperature. Since the room temperature was near about *T* and the volume of the manometer above the water level was very small, the error introduced may safely be neglected.

TABLE X.

Effect of varying the concentration of hydrogen peroxide.

Temp.$=25°$. $p_H=1·26$. H.Q.$=0·025M$. Na-tungstate$=0·01M$.

$H_2O_2(M)$ ...	0·18	0·36	0·54	0·72	1·08
K ...	0·00067	0·00088	0·00106	0·0012	0·0014

$1/K$ plotted against 1/conc. of H_2O_2 gives approximately a straight line (*cf.* Fig. 2).

TABLE XI.

Effect of varying the concentration of sodium tungstate.

Temp.$=25°$. $p_H=1·26$. $H_2O_2=0·72M$. H.Q.$=0·025M$.

Na-tungstate (M) ...	0·005	0·01	0·015	0·02
K ...	0·00068	0·0012	0·00165	0·00204

TABLE XII.

Effect of varying the p_H.

Temp.$=25°$. H.Q.$=0·025M$. $H_2O_2=0·72M$. Na-tungstate$=0·01M$.

p_H ...	1·26	1·7	2·25	3·1	4·1	5·1
K ...	0·0012	0·00122	0·0012	0·00119	0·00118	0·00126

At p_H 5·1, we used acetate buffer at suitable concentration so that it did not cause any decomposition of hydrogen peroxide. It has got no influence of its own on the activity of the sol.

TABLE XIII.

Effect of varying the temperature.

$p_H=1·26$. $H_2O_2=0·72M$. Na-tungstate$=0·01M$.

Temp.	Conc. of H.Q.	K.	Temp.	Conc. of H.Q.	K.
25°	0·0125M	0·00121	25°	0·025M	0·0012
35°	0·0125.	0·00268	35°	,,	0·0029

The temperature coefficient of the reaction is $Q_{10}=2·4$ to $2·5$.

TABLE XIV.

Influence of potassium cyanide.

Temp.=25°. p_H=4·1. H.Q.=0·025*M*. H_2O_2=0·72*M*.

Conc. of Na-tungstate.	Conc. of KCN.	*K*.
0·01*M*	...	0·0012
0·01	0·0025*M*	0·0012
0·01	0·005	0·00119

Potassium cyanide has got no influence on the catalytic activity of the sol.

B. Oxidation of Hydroquinone by means of Hydrogen Peroxide in Presence of Molybdic Acid Sol.

In the case of molybdic acid sol the experimental procedure is exactly the same as in the case of tungstic acid sol. The products of reaction are exactly the same with both the sols. The velocity of the oxidation of hydroquinone to quinone can be measured in exactly the same way as the tungstic acid sol. The results of kinetic measurements of the oxidation of quinone to CO_2 and maleic acid are given below. The velocity coefficient is determined in exactly the same way as the tungstic acid sol.

TABLE XV.

Effect of varying the concentration of hydroquinone.

Temp.=25°. p_H=1·12. H_2O_2=0·72*M*. Am. molybdate=0·02*M*.

H.Q. (*M*)	...	0·0083	0·0125	0·0166	0·025	0·033
K (mean)	...	0·00135	0·00131	0·0013	0·00132	0·00127

TABLE XVI.

Effect of varying the concentration of H_2O_2.

Temp.=25°. p_H=2·5. H.Q.=0·025*M*. Am. molybdate=0·005*M*.

H_2O_2(*M*)	...	0·18	0·36	0·54	0·72	1·08
K	..	0·00114	0·00117	0·00119	0·00122	0·00128

The velocity constant is practically independent of the concentration of hydrogen peroxide.

TABLE XVII.

Effect of varying the concentration of Am. molybdate.

Temp. = 25°. $p_H = 1{\cdot}12$. H.Q. = 0·025*M*. $H_2O_2 = 0{\cdot}72M$.

Am molybdate (*M*) ...	0·01	0·015	0·02	0·025
K ...	0·00069	0·00099	0·0013	0·0016

TABLE XVIII.

Effect of varying the p_H.

Temp. = 25°. H.Q. = 0·025*M*. $H_2O_2 = 0{\cdot}72M$. Am. molybdate = 0·02*M*.

p_H ...	1·12	1·51	1·85	2·1	3·1	4·2	5·0
K ...	0·0013	0·00194	0·00225	0·00268	0·0030	0·00314	0·0032

The velocity constant increases as the p_H increases.

TABLE XIX.

Effect of varying the temperature.

$p_H = 1{\cdot}12$. $H_2O_2 = 0{\cdot}72M$. Am. molybdate = 0·02*M*.

Temp.	Conc. of H.Q.	*K*.	Temp.	Conc. of H.Q.	*K*.
25°	0·0125*M*	0·00133	25°	0·025*M*	0·0013
35	"	0·0027	35	"	0·00272

The temperature coefficient of the reaction is about 2. The reaction can similarly be carried out in presence of vanadic acid sol.

C. Oxidation of Pyrogallol by means of Hydrogen Peroxide in Presence of Tungstic Acid Sol.

The oxidation of pyrogallol in presence of peroxidase has been carried out by many workers. Prof. Willstätter and co-workers (*Annalen*, 1918, **416**, 21 ; 1923, **430**, 269 ; 1926, **449**, 156, 175) have studied the preparation, purification and activity of peroxidases derived from different sources. They studied the peroxidase activity by oxidising pyrogallol and estimating the quantity of purpurogallin formed. Rice and Hanzawa (*Ind. Eng. Chem.*, 1922, **14**, 201) have investigated the peroxidase activity in milk by oxidising pyrogallol in presence of hydrogen peroxide. Getchell and Walton (*J. Biol. Chem.*, 1931, **91**, 419) have studied the influence of some factors on the activity of peroxidase in the oxidation of pyrogallol to purpurogallin.

Many other similar works have been carried out for the determination of peroxidase activity by oxidising pyrogallol. Purpurogallin is obtained by the oxidation of pyrogallol in presence of low concentrations of tungstic acid sol and hydrogen peroxide. In this paper, experiments were carried out to compare the activity of tungstic acid sol with peroxidases using pyrogallol as substrate.

Isolation of Purpurogallin.

Pyrogallic acid (5 g.) was dissolved in 150 c. c. of redistilled water and filtered. 0·1 *M*-sodium tungstate (2 c. c.) in the form of sol was added. A dilute solution of hydrogen peroxide was then added in small quantities at a time. When the addition of hydrogen peroxide was complete, the reaction mixture was cooled in ice. Purpurogallin was separated, filtered, washed and then dried. It was then recrystallised from ether, yield 0·4 g.

A pure sample of pyrogallic acid was taken and dissolved in conductivity water. A fresh solution of pyrogallic acid was prepared daily. Merck's perhydrol was used for preparing fresh solution of hydrogen peroxide. The reaction was carried out at 30° in a Pyrex conical flask in which pyrogallol, hydrogen peroxide and sol were added, the total volume being made 50 c.c. Pyrogallol was oxidised to purpurogallin which could be easily extracted with ether.

In the case of oxidation with peroxidase, the reaction has been arrested after a period of ten to twelve minutes by the addition of suitable inhibitors such as strong hydrochloric acid, strong sulphuric acid, mercuric chloride and potassium cyanide. But in the case of sol as no such suitable inhibitor is available to stop the reaction, we had necessarily to prolong the time of measurement. One hour reaction period was found to be most suitable under the prevailing experimental conditions. Purpurogallin formed was twice extracted with ether in a seperating funnel, first with 15 c.c. and then with 10 c.c. As the dye thus extracted was not absolutely pure but contained slight amount of colouring matter, the combined extract was washed with 10 c.c. of distilled water three or four times. By this means a very pure pigment was obtained. The volume of the extract was then made 20 c.c. and the value of log $\tan\theta_1/\tan\theta$ was obtained spectrophotometrically at wave-lenghth 525 $\mu\mu$. The thickness of the solution used was 4 cm.

The previous workers have estimated the amount of purpurogallin formed, by comparing the extract colorimetrically with a standard. But the present author has found that a great saving of time and trouble can be effected by estimating it spectrophotometrically.

FIG. 3.

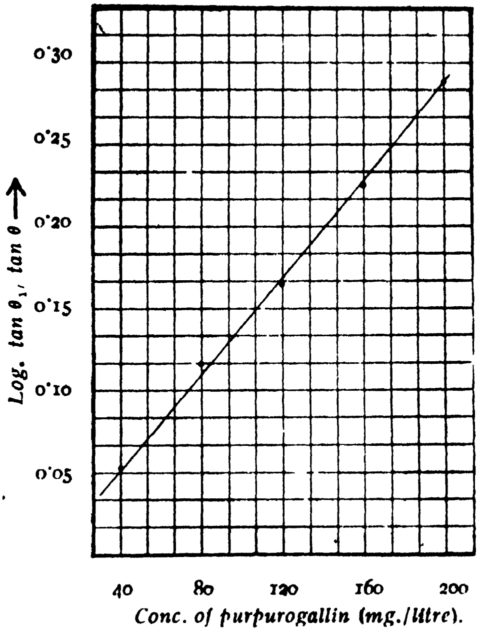


TABLE XX.

Purpurogallin (mg./litre).	Log $\frac{\tan \theta_1}{\tan \theta}$.
40	0·0536
80	0·1164
120	0·1655
160	0·2259
200	0·2875

Table XX gives the values of log tan θ_1 /tan θ for various concentrations of purpurogallin at wave-length 525$\mu\mu$, the thickness of the solution used being 4 cm. In this region of the spectrum Beer's law is obeyed as shown in Fig. 3, where the values of log tan θ_1 /tan θ plotted against concentration give a stright line. From the readings in the spectrophotometer for the above wave-length, it is obvious that the concentration of an unknown solution can conversely be calculated. Purpurogallin was prepared by the method of Perkin and Steven (*J. Chem. Soc.*, 1903, **83**, 192) and was recrystallised from alcohol and ether. The results are tabulated below.

TABLE XXI.

Effect of varying the concentration of pyrogallol.

Temp. = 30°. p_H = 4·3. $H_2O_2 = 8 \times 10^{-3} M$. Na-tungstate = $10^{-4} M$.

Pyrogallol (mg./c.c.) ...	0·5	1	2	3	
Pupurogallin (mg./litre) ...	0·71	105	160	200	228

TABLE XXII.

Effect of varying the concentration of H_2O_2.

Temp. = 30°. p_H = 4·3. Na-tungstate = $10^{-4}M$. Pyrogallol = 1 mg./c.c.

$H_2O_2(M)$ ...	2×10^{-3}	4×10^{-3}	8×10^{-3}	$1{\cdot}2\times10^{-2}$	$1{\cdot}6\times10^{-2}$	2×10^{-2}
Purpurogallin (mg./litre) ...	77	88	105	124	135	135

TABLE XXIII.

Effect of varying the concentration of catalyst.

Temp. = 30°. p_H = 3·1. $H_2O_2 = 4\times10^{-3}M$. Pyrogallol = 1 mg./c.c.

Na-tungstate ...	5×10^{-5}	10^{-4}	2×10^{-4}	3×10^{-4}
Purpurogallin (mg./litre) ...	33	66	124	180

TABLE XXIV.

Effect of varying the p_H.

Temp. = 30°. $H_2O_2 = 4\times10^{-3}M$. Na-tungstate = $10^{-4}M$.
Pyrogallol = 1 mg./c.c.

p_H ...	2·8	3·1	3·5	4·3	5·3	6·3
Purpurogallin (mg./litre) ...	54	65	77	88	147	100

TABLE XXV. TABLE XXVI.

Temperature coefficient.

Table XXV. $H_2O_2 = 4\times10^{-3}M$. Na-tungstate = $10^{-4}M$. p_H = 4·3.

	Pyrogallol = 1 mg./c.c.		Pyrogallol = 4 mg./c.c.	
Temp.	20°	30°	20°	30°
Purpurogallin (mg./litre)	27	88	50	150

Table XXVI. Pyrogallol = 4 mg./c.c. $H_2O_2 = 4\times10^{-3}M$. Na-tungstate = $2\times10^{-4}M$. p_H = 4·2.

Temp.	10°	20°
Purpurogallin (mg./litre)	44	106

TABLE XXVII.

Effect of salts.

Temp. = 30°. $H_2O_2 = 4 \times 10^{-3} M$. $p_H = 3{\cdot}1$. Pyrogallol = 1 mg./c.c.

Salt.	Conc. in the reaction mixture.	Na tungstate.	Purpurogallin (mg./litre).
—	—	$10^{-4} M$	66
$HgCl_2$	$10^{-3} M$	10^{-4}	66
KCN	10^{-4}	,,	66

Oxidation of pyrogallol can similarly be carried out in presence of molybdic and vanadic acids.

D. Oxidation of Guaiacol by means of Hydrogen Peroxide in Presence of Tungstic Acid Sol.

The oxidation of *ortho*-cresol and guaiacol has been extensively carried out in presence of oxidases, peroxidases and other metallic salts (Bertrand, *Compt. rend.*, 1903, **137**, 1266; Bansi and Ucko, *Z. physiol. Chem.*, 1926, **157**, 192; 1927, **164**, 52; **169**, 177).

According to Bertrand, guaiacol is oxidised in presence of laccase to a red compound tetraguaiacoquinone according to the following equation,

$$4\ C_6H_4OH\ (OCH_3) + 2\ O_2 = 4\ H_2O + \begin{array}{l} C_6H_3(OCH_3)-O-O-C_6H_3(OCH_3) \\ \\ C_6H_3(OCH_3)-O-O-C_6H_3(OCH_3) \end{array}$$

(Tetraguaiacoquinone).

Peroxidase acts as laccase in presence of hydrogen peroxide.

Tetraguaiacoquinone is a fine crystalline powder having a purplish-red colour with a faint green metallic lustre. It is insoluble in water, slightly soluble in ether and a little less so in alcohol, still less so in benzene and readily soluble in chloroform giving a red colour. It is also soluble in alkalis forming coloured solutions.

With low concentrations of tungstic acid sol and hydrogen peroxide, the oxidation of guaiacol proceeds similarly and the product of oxidation can be easily extracted with chloroform.

The oxidation of guaiacol was carried out in exactly the same manner as the oxidation of pyrogallol and hydroquinone, at 25 . The solution of guaiacol was prepared in redistilled water. The reaction was carried out in Pyrex conical flask in which guaiacol, hydrogen peroxide and sol were added, the total volume being made 25 c.c. After the required time interval, the entire mixture was extracted with 25 c.c. of chloroform, leaving the reaction mixture colourless. The red chloroformic solution was then washed with water. The volume was made upto 25 c.c. and log tan $\theta_1/\tan\theta$ determined. With the progress of the reaction, the depth of the colour of the chloroformic solution increased which was followed by the rotation of the angle in the König-Marten spectrophotometer. All measurements were made at wave-length 525 $\mu\mu$ in a glass cell, the thickness of the solution being 1 cm. The experiments were all repeated and reproducible results were obtained. The results of kinetic measurements are represented graphically by plotting log tan $\theta_1/\tan\theta$ against time. Table XXVIII gives the results of a typical experiment in detail.

Fig. 4.

Effect of varying the conc. of reducing substrate.

Conc. of $H_2O_2 = 0.036M$.
Na-tungstate $= 0.002M$. $p_H = 4.4$. $t = 24$.

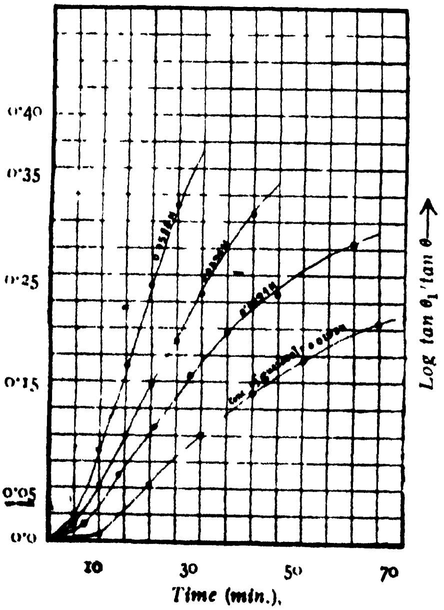


Fig 5.

Influence of hydrogen peroxide.

Guaiacol $= 0.0198M$.
Na-tungstate $= 0.002M$.
$p_H = 4.4$. Temp. = 25°.

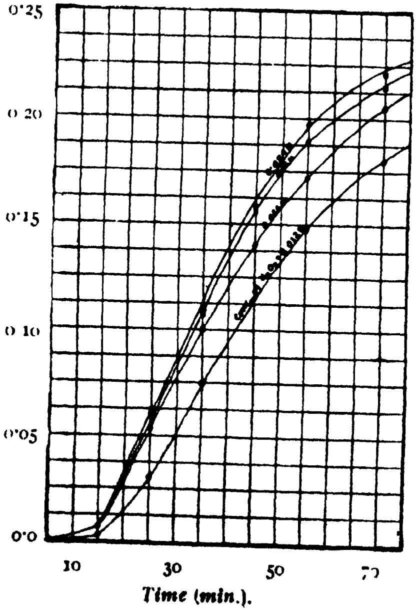


Fig. 6.

Influence of hydrogen number.

Guaiacol $= 0{\cdot}0198M$. $H_2O_2 = 0{\cdot}012M$. Na-tungstate $= 0{\cdot}002M$.
Temp. $= 25^\circ$.

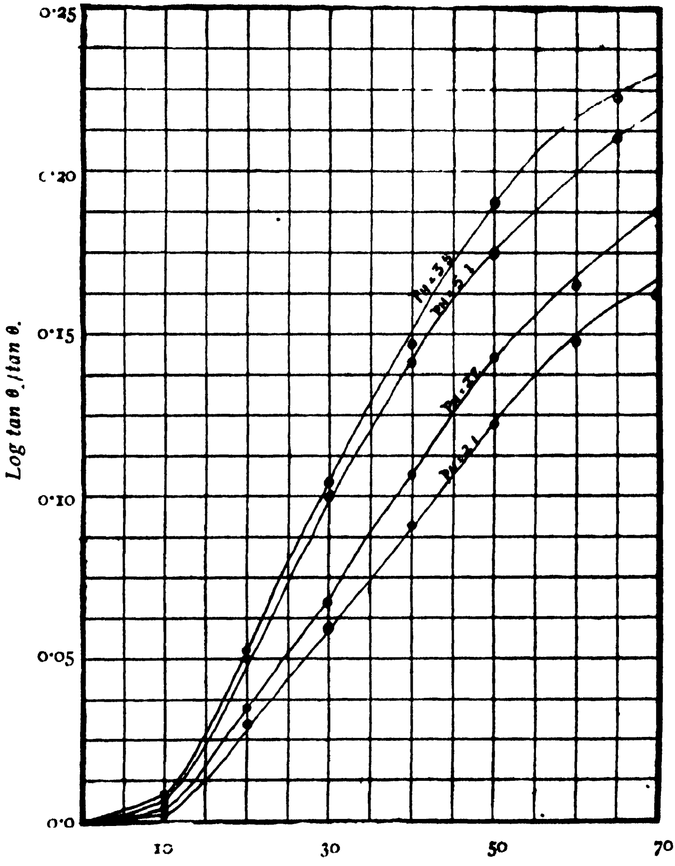


TABLE XXVIII.

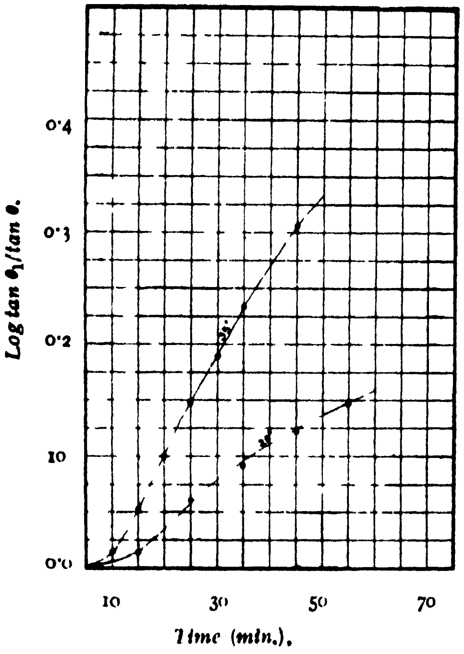
Temp. $= 25^\circ$. $p_H = 4{\cdot}4$ $H_2O_2 = 0{\cdot}036M$. Na-tungstate $= 0{\cdot}002M$. Guaiacol $= 0{\cdot}0588\,M$. Composition of the reaction mixture = 20 c.c. guaiacol soln. + 1 c.c. water + 2 c.c. sol +' 2 c. c. H_2O_2.

Time	...	0	5	10	15	20	25	30
Spectrophotometric readings	...	46	47·5	51·5	56·5	61	65	68·5
Log tan θ_1/tan θ	...	—	0·02279	0·08423	0·16406	0·24109	0·31617	0·38944

Effect of varying the temperature.

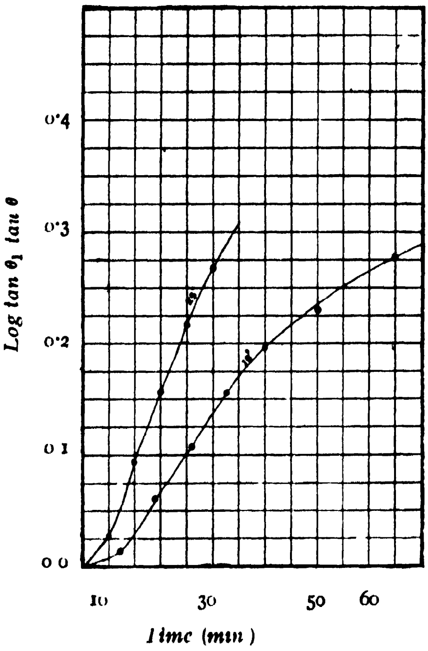
Guaiacol = 0·0396M. H_2O_2 = ·036M.
Na-tungstate = ·002M. p_H = 4·4.

Fig. 7a.



Guaiacol = ·0294M. H_2O_2 = ·036M.
Na-tungstate = 0·02M. p_H = 4·4.

Fig. 7b.

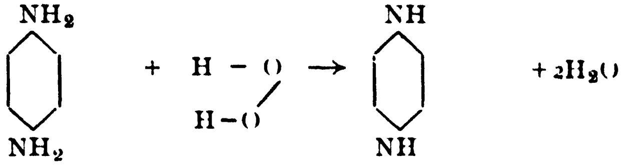


The reaction can similarly be carried out in presence of molybdic acid sol and vanadic acid sol.

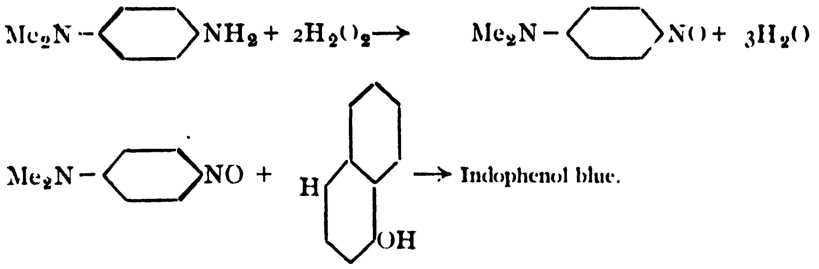
E. Oxidation of α-Naphthol and p-Phenylenediamine Mixture by Hydrogen Peroxide in Presence of Tungstic Acid Sol.

A mixture of α-naphthol and *p*-phenylenediamine or the so-called Nadi reagent has been extensively oxidised to measure the activities of oxidases, peroxidases, and other heavy metals as iron and copper (Guthrie, *J. Amer. Chem. Soc.*, 1931, **53**, 242; Harrison, *Biochem. J.*, 1929, **23**, 982; Wertheimer, *Fermentforsch.*, 1926, **8**, 497).

p-Phenylenediamine on oxidation gives the corresponding dark purple di-imino compound



while in the case of Nadi reagent containing an equimolecular mixture of dimethyl-*p*-phenylenediamine and α-naphthol, the reaction consists in the oxidation of the diamine compound to a nitroso compound and the condensation of the latter with α-naphthol forming indophenol blue.



The same end-products were obtained by replacing the oxidases or the peroxidases with tungstic acid sol.

A solution of *p*-phenylenediamine (0·1%) and a solution of α-naphthol of same strength were prepared fresh every day and filtered. The reaction was carried out in a Pyrex conical flask in which the reactants and the sol were added in suitable concentrations, the total volume being made 25 c.c. The flask was then immersed in a thermostat at 30°. At timed intervals the entire mixture was extracted with 25 c.c. of toluene leaving the reaction mixture colourless. No appreciable amount of spontaneous oxidation took place in presence of hydrogen peroxide alone at these intervals. The total volume was then made up to 25 c.c. and the spectrophotometric reading taken at wave-length 525 $\mu\mu$, the thickness of the solution used being 0·5 cm. It has been found that the velocity coefficient of the reaction can be determined approximately by means of the equation

$$K = \frac{\log \tan \theta_2 - \log \tan \theta_1}{d(t_2 - t_1)}$$

where θ_2 is the spectrophotometric reading corresponding to the time t_2 and θ_1 corresponding to the time t_1, d being the thickness of the solution in mm. Indophenol in toluene solution has been found to obey the Beer's law at wave-length 525 $\mu\mu$. The results are tabulated below.

TABLE XXIX.

Effect of varying the concentration of reducing substrate.

H_2O_2=0·02*M*. Na-tungstate=0·002*M*. p_H =5. Temp.=30°.

p-Phenylenediamine in c.c. (0·1% solution filtered) ...	2	4	6	8
α-Naphthol in c.c. (0·1% solution filtered) ..	2	4	6	8
K(mean) ...	0·0015	0·003	0·0046	0·0064

TABLE XXX.

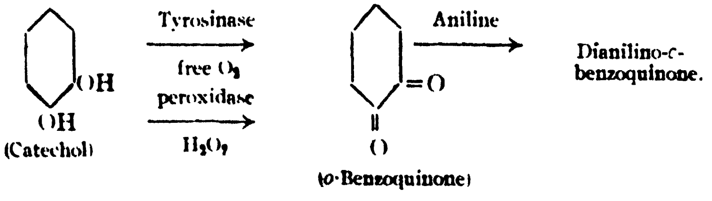
Effect of varying the concentration of hydrogen peroxide.

Na-tungstate=0·002*M*. p_H =5. Temp.=30°. *p*-Phenylenediamine =4 c.c. α-Naphthol=4 c.c.

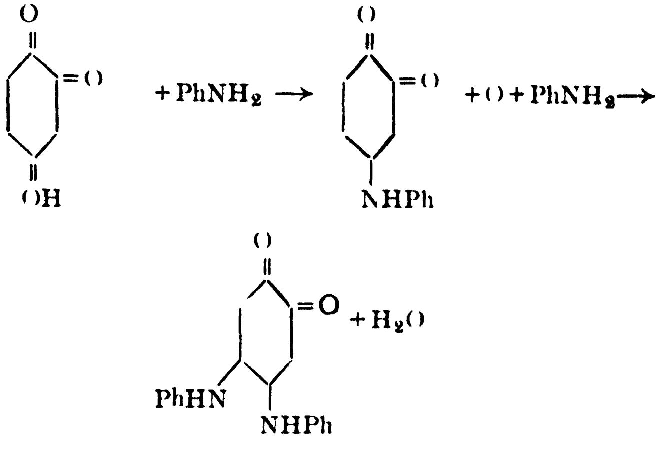
H_2O_2(*M*) ..	0·005	0·01	0·02	0·03	0·05
K ...	0·0028	0·0029	0·003	0·00315	0·0032

F. *Oxidation of Catechol,* p-*Cresol, and other Phenols by means of Hydrogen Peroxide in Presence of Tungstic Acid Sol.*

Catechol, phenol, *m*- and *p*-cresol have been oxidised by tyrosinase and peroxidase with the formation of *ortho*-quinone by Pugh and Raper (*Biochem. J.*, 1927, **21**, 1370). *o*-Quinones are very unstable substances and have been isolated as dianilinoquinones by carrying out the reactions in presence of aniline. The reactions with catechol have been represented as follows:



But quite recently it has been suggested by Wagreich and Nelson (*J. Biol. Chem.*, 1936, **116**, 459) that in the oxidation of catechol by tyrosinase, it is not *o*-quinone but a hydroxy derivative of it which reacts with aniline forming dianilinoquinone according to the equation



(Dianilino-*o*-benzoquinone).

Dianilino-o-benzoquinone as described above can also be isolated by the oxidation of catechol in presence of tungstic acid sol and hydrogen peroxide by the method of Pugh and Raper as given below.

Catechol (25 g.) and aniline (5 c.c.) were dissolved in a litre of water. Hydrogen peroxide (20 c.c., 5%) and 0·05M-sodium tungstate (10 c c.) in the form of sol were added. After some time a red precipitate was obtained which after 3 days, was filtered off, washed with 1% hydrochloric acid to remove excess of aniline and then with water It was dried *in vacuo* and extracted in a Soxhlet apparatus with acetone On evaporation of the acetone solution, bright red needles seperated out. It was further purified by recrystallisation from acetone, m.p. 191°, yield, 1 g ; other properties were identical with those of the product obtained by Pugh and Raper (*loc. cit.*).

Dianilinohomoquinone-anil ($C_{25}H_{21}ON_3$) can similarly be isolated from *p*-cresol, but the yield of pure product is small, some tarry substance also being produced. Attempts were made to isolate similar anilino-compound from tyrosine but were not successful. This is probably due to the fact that the *o*-quinone derived from tyrosine undergoes further reaction, *i.e.*, form indole derivative (Raper, *Biochem. J.*, 1927, **21**, 89).

From the above, it is evident that *o*-quinones are produced by the action of tungstic acid sol and hydrogen peroxide on *p*-cresol and catechol.

All phenolic substances can be oxidised by means of hydrogen peroxide in presence of sodium tungstate or tungstic acid sol, ammonium molybdate or molybdic acid sol and vanadic acid, finally with the production of carbon dioxide.

Tincture of guaiacum has been extensively used in the detection of peroxidases. In presence of peroxidases and hydrogen peroxide it turns blue. Replacing the peroxidases by sols, the same blueing of guaiacum takes place.

G. Oxidation of Tyrosine and Tryptophan by means of Hydrogen Peroxide in Presence of Tungstic Acid Sol.

The oxidation of tyrosine and tryptophan which are substances of metabolic interest and are widely distributed in animal and plant organisms, have been carried out by many workers in presence of tyrosinase and peroxidase with the formation of coloured products. The problem of finding out the mechanism of oxidation of tyrosine by tyrosinase is a long-standing one and the exact nature of tyrosinase whether it consists of a single enzyme or a mixture of different enzymes has not yet been elucidated. All attempts to separate tyrosinase into components have hitherto failed.

Various theories have been put forward from time to time to explain the course of oxidation of tyrosine by tyrosinase. Bach (*Biochem. Z.*, 1914, **60**, 221) suggested that the initial action of tyrosinase on tyrosine could be represented as

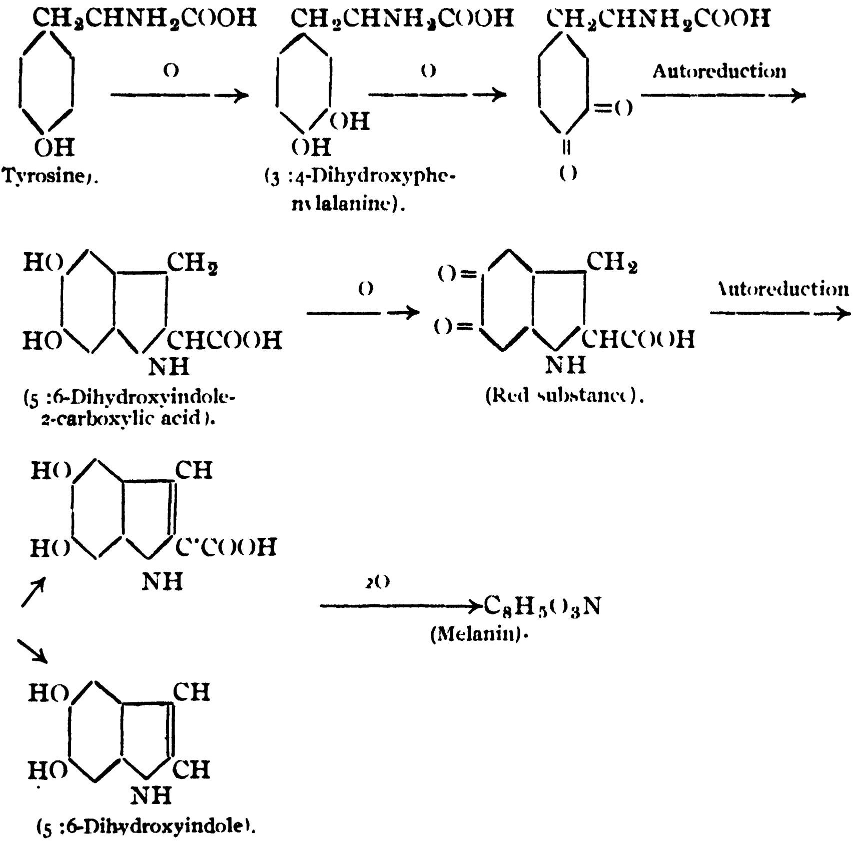
$$\underset{\text{(Tyrosine)}}{OH{\cdot}C_6H_4{\cdot}CH_2CH{\cdot}NH_2COOH} + H_2O + A \text{ (Hydrogen acceptor)}$$

$$= \underset{\text{(p-Hydroxyphenyl acetaldehyde)}}{OH{\cdot}C_6H_4CH_2CHO} + NH_3 + CO_2 + AH_2.$$

Folpmers (*Biochem. Z.*, 1916, **78**, 180) showed that the first action of tyrosinase on tyrosine was the production of ammonia and a hydroxyaldehyde by the action of a deamidase according to the equation

$$OH{\cdot}C_6H_4CH_2CH{\cdot}NH_2COOH + O = OH{\cdot}C_6H_4CH_2CHO + NH_3 + CO_2.$$

The second ferment causes a further oxidation of the aldehyde (or its condensation product with ammonia) to a black pigment melanin. In the case of phenylglycine, the author succeeded in actually demonostrating the presence of a deamidase in that he isolated benzaldehyde in the form of its *p*-nitrophenylhydrazone. All other theories put forward held that ammonia was the first product in the oxidation of tyrosine by tyrosinase. Recently the course of oxidation of tyrosine by tyrosinase has been extensively studied by Prof. Raper and his pupils. The scheme of the reaction postulated by them may be represented as follows :



From the above scheme it is evident that five atoms of oxygen are necessary per molecule of tyrosine to convert it into melanin (Dulière and Raper, *Biochem. J.*, 1930, **24**, 237) and at no stage of the reaction is nitrogen split off in the form of ammonia as supposed by other authors, the initial nitrogen atom being present in melanin.

Now it has been found that the behaviour of tyrosinase towards tyrosine and other phenols can be simulated by tungstic acid and molybdic acid sol in presence of hydrogen peroxide. Tyrosinase acts on tyrosine and some other monohydric and dihydric phenols. Phenylalanine which differs from tyrosine only in this respect that it does not contain any phenolic hydroxyl group, is not attacked by tyrosinase. Similar is the case with tungstic acid and molybdic acid sols. They attack all monohydric and dihydric phenols with the formation of coloured products but not phenylalanine. Though *o*-dihydroxy derivative is produced by the action of tyrosinase on tyrosine (Raper, *Biochem. J.*, 1926, **20**, 735) which is then converted into *o*-quinone, the *o*-quinone can not be isolated as aniline compound as can be done with other phenols (Pugh and Raper, *Biochem. J*, 1927, **21**, 1370). This is due to further reaction, *i.e.*, the formation of indole derivative from tyrosine. Similar is the case when the tyrosinase is replaced by sol and hydrogen peroxide. No aniline compound could be isolated. It has been shown by Happold and Raper (*Biochem J.*, 1925, **19**, 92) and Robinson and McCance (*ibid.*, 1925, **19**, 251) that the system phenol-tyrosinase can bring about the deamination of an amino-acid added to the system. This has been explained by Happold and Raper to be due to the formation of an *ortho*-quinone which attacks the amino-acids. But it has been shown by Robinson and McCance (*loc. cit.*) that tyrosine is unable to bring about the external oxidation of amino-acids as *p*-cresol and other phenols do. The author in a subsequent paper (to be published shortly) has shown that in the above system tyrosinase can be replaced by sol-hydrogen peroxide with the same results but no deamination takes place when tyrosine is used instead of *p*-cresol. Melanin, a black pigment, has been isolated as the end-product in the oxidation of tyrosine by tyrosinase. At low concentrations of sol and hydrogen peroxide a black pigment containing 10-15% inorganic matter as impurities has been isolated from tyrosine. But when the concentrations of sol and hydrogen peroxide are increased, both tyrosine and tryptophan are oxidised with the production of carbon dioxide, ammonia and other products, the nature of which is in the course of investigation.

From the above, it is clear that there is a similarity in the behaviour of tyrosinase and sol-hydrogen peroxide towards tyrosine but with high concentration of hydrogen peroxide ammonia is produced So experiments were carried out to show whether this deamination of tyrosine takes place during the first stages of the reaction as supposed by Bach, Folpmers and others in the case of tyrosinase. The results were found to be entirely negative. The black pigment that has been isolated is found to be free from any ammonia. When treated with sol-hydrogen peroxide it gives ammonia and carbon dioxide showing that ammonia is not the initial product of reaction. Further investigations to determine the course of the reaction are in progress.

Ammonia.—Ammonia was determined at various stages of the reaction by the method of Whitehorn (*J. Biol. Chem.*, 1923, **56**, 751). Tyrosine (Pfansteihl, 0·2 g.) was dissolved in a minimum quantity of hydrochloric acid and the volume made up to 100 c.c. The solution was then brought to a p_H 4 to 5. Hydrogen peroxide (5 c.c., 3 molecules of hydrogen peroxide for each molecule of tyrosine) and 10 c.c. of sol (6 c.c., 0·05*M*-Na_2WO_4) were added and the ammonia was determined by the above method. The process consists in filtering the solution through a layer of permutite. About 5 c.c. of finely granular permutite were placed in uniform layer in the funnel of a Witt's apparatus connected with a water-pump. The permutite layer was then washed with 2% acetic acid to neutralise any alkali present and then several times with distilled water to remove the traces of acetic acid. When the reaction mixture containing ammonia was filtered, it was washed with 15 to 20 c.c. of distilled water four to five times. The permutite containing ammonia was then removed to a test tube and 8 c.c. of a 10% solution of sodium hydroxide added and shaken for a minute. It was then filtered and in the filtrate ammonia was estimated by modified Nessler's solution (Bock and Benedict formula). In the above reaction mixture no ammonia could be detected at any stage. Test estimations in which 0·5 to 1 mg. of ammonia was initially added, showed that the added amounts could be estimated almost quantitatively. But when excess of hydrogen peroxide (4 c.c., Merck's perhydrol) was added in the above mixture, the presence of ammonia could be easily detected after 24 hours.

Isolation of the Black Pigment.—Tyrosine (1 g.) was dissolved in minimum quantity of strong HCl and the volume made up to 100 c.c. Hydrogen peroxide (10 c.c., 5 molecules of hydrogen peroxide for every molecule of tyrosine) and 15 c.c. of sol (10 c.c., 0·05 *M*-Na_2WO_4) were added. After standing for two to three days a deposit of black pigment was obtained at the bottom of the solution. The supernatant clear solution was removed as far as practicable without disturbing the precipitate. It was then purified by boiling with successive quantities of dilute hydrochloric acid and finally washed with hot water by decantation for 15 to 20 times. After filtration it was washed again and dried in a vacuum desiccator containing sulphuric acid. On analysis it was found to contain 10 to 15% ash and nitrogen was present in sufficient quantity as shown by qualitative test

In presence of milk poroxidase and H_2O_2 both tyrosine and tryptophan are oxidised (Elliot, *Biochem. J.*, 1932, **26**. 10) while in presence of plant peroxidase only tyrosine is oxidised and tryptophan is not (*Biochem. J.* 1932, **26**, 1281). With tungstic acid and molybdic acid sols both tyrosine and tryptophan are oxidised, the former more easily than the latter.

The velocity of the first partial process of the above reaction has been studied by Raper and Wormall (*Biochem. J.*, 1923, **17**, 454) and has been found to be of monomolecular type. The velocity coefficients are approximately constant throughout the reaction.

DISCUSSION.

Below is given a comparison of the results obtained by the oxidation of phenolic substances in presence of peroxidase and tungstic acid sol by means of hydrogen peroxide.

(1) At low concentration of hydrogen peroxide, the products of reaction are same in both cases.

(2) In the case of peroxidase, as the concentration of reducing substrate is increased, the amount of the product of reaction increases upto a certain value depending on the experimental conditions and then begins to decrease (*cf.* Getchell and Walton, *J. Biol. Chem.*, 1931, **91**, 419 ; Dey and Sitharaman, *J. Indian Chem. Soc.*, 1932, **9**, 499). But in the case of tungstic acid sol as the concentration of the oxidisable substances increases, the amount of the product of reaction increases but the relation is not linear,

(3) In the plant peroxidase reactions, the activity of the peroxidase increases with increase in the concentration of hydrogen peroxide but excess of hydrogen peroxide retards the activity and in large quantities destroys it altogether (*Ber.*, 1904, **37**, 3787; *Annalen*, 1926, **449**, 175). But peroxidasic action of oxyhæmoglobin, contrary to that of plant peroxidase, increases pronouncedly with rising H_2O_2 concentration and is different in different kinds of animals. With tungstic acid sol, the activity of the sol slowly increases upto a certain value and further increase of hydrogen peroxide has very little influence.

(4) The increase in the concentration of both peroxidase and sol influences the reaction velocity but not in strict proportion to their increase in concentration.

(5) With pyrogallol substrate and horse-radish peroxidase the optimum p_H has been given as 7 by Bansi and Ucko (*Z. physiol. Chem*, 1926, **159**, 235). With hydroquinone substrate and "Chow chow" peroxidase, the optimum p_H lies between 4·8 and 5·2 (Dey and Sitharaman, *loc. cit.*). The optimum p_H for the oxidation of guaiacol is between p_H 5 and 5·2 (Bansi and Ucko, *loc. cit.*). But with sol and pyrogallol the optimum p_H is 5·3 and with guaiacol the optimum p_H is 3·5.

(6) In the twelve minutes' reaction period, the weight of purpurogallin formed at 10° is 140% of that formed at 0°, and at 20°, 120%

of that formed at 10°. From this, the temperature coefficient is given to be 1·4 in the 0-10° range, and 1·2 in the 10-20° range by Getchell and Walton (*loc. cit.*) The temperature coefficient in the case of sol and pyrogallol is 2·4 in the 10-20° range and 3·1 in the 20-30° range.

(7) Potassium cyanide and mercuric chloride are strong poisons to peroxidases but they have got practically no influence upon the sol.

(8) Most of the peroxidases are heat-labile except the pseudo-peroxidases which are thermostable. The sol is heat-stable and in this respect it resembles the pseudo-peroxidases.

(9) Ultraviolet light is very active in destroying the activity of the peroxidase (*Biochem. Z.*, 1931, **241**, 384; *Compt. rend.*, 1911, **153**, 979). But in the case of the sol the reverse case is found. Many photochemical reactions are being carried out in our laboratory in presence of the sol.

The mechanism of the oxidation of phenols by hydrogen peroxide in presence of tungstic acid, molybdic acid and vanadic acid sols can be explained by the per-acid formation theory as has been done in the case of sulphydryl compounds.

But Fernandes (*Atti. R. Acad. Lincei*, 1925, **1**, 439; *Gazzetta*, 1925, **55**, 424) has shown that organic compounds containing two hydroxyl groups in the *ortho* position react to give complex derivatives with salts of molybdic, tungstic and uranic acids. He has isolated two series of compounds according to the conditions and proportions of substances employed. The two series are

$$\left[\begin{matrix} & Z \\ XO_3 & \\ & H_2O \end{matrix}\right]^{R}_{R} \quad \text{and} \quad \left[\begin{matrix} & Z \\ XO_2 & \\ & Z \end{matrix}\right]^{R}_{R}$$

where X = Mo, W, or U; R = H, K, Na, Tl, guanidine, or pyridine; $Z = C_6H_4O_2$ or $C_6H_4O_3$.

Compounds of neither type are formed by either di- or trihydroxylated compounds unless at least two hydroxyl groups occupy *ortho* position to one another, such relationship being necessary for the development of co-ordination valency.

The author also has prepared similar complexes of pyrocatechol and pyrogallol with salts of tungstic acid and molybdic acid, and has studied their reactions with hydrogen peroxide. It has been found that they also react with hydrogen peroxide with the production of carbon dioxide. The mechanism of the reaction can be explained as follows.

When salts of tungstic acid and molybdic acid are allowed to react with *ortho*-dihydroxy compounds, they oxidise the hydroxy compounds to the corresponding quinones forming a complex. When hydrogen peroxide is added, the reduced salts are oxidised and the complex is dissociated. They then react with hydrogen peroxide forming per-salts which further oxidise the quinones with the production of carbon dioxide.

About the mechanism of peroxidase action, majority of opinions favour the formation of an active enzyme-substrate complex between the peroxidase and hydrogen peroxide (Willstätter and Weber, *Annalen*, 1926, **449**, 156) and the view that the reducing substrate also combines with the enzyme has not hitherto been accepted (Haldane, "Enzymes," 1930 Ed.). Willstätter and Weber found that excess of hygrogen peroxide decreases the activity of peroxidase and ultimately inhibits the reaction. This inactivation may be combated either by increasing the concentration of reducing substrate or by decreasing the concentration of hydrogen peroxide by means of catalase To explain this phenomenon they suggested that the peroxidase reacts with hydrogen peroxide forming two additive compounds corresponding to the formulae $HO-OH$ and $H_2O=O$ for hydrogen peroxide. At low concentration of hydrogen peroxide it combines with the peroxidase in the form $H_2O=O$ to give a compound which is catalytically active and in high concentration it combines as $HO-OH$ to give a compound which is relatively inactive and requires a high concentration of reducing substrate for its decomposition.

As the above explanation is unsatisfactory in explaining all the observed facts, recently a theory has been put forward by Mann (*Biochem. J.*, 1931, **25**, 918) and by Woolf (*ibid.*, 1931, **25**, 342) in which they have put forward the hypothesis that all the substrates must be combined at the enzyme before catalysis can take place. Both the reducing substrate and hydrogen peroxide combine at their respective groups which are moderately specific. But when hydrogen peroxide is in excess, it combines with the nonspecific group keeping the reducing substrate away and hence causing inhibition. This inhibition may be combated either by increasing the concentration of reducing substrate or by destroying the H_2O_2 by means of catalase as shown by Willstätter and Weber (*loc. cit.*). Similar conclusion has been drawn by Balls and Hale (*J. Biol. Chem.*, 1934, **107**, 787) from a study of the inhibition and specificity of peroxidase.

Shibata (*Acta Phytochim Japan*, 1929, **4**, 373) from a study of the complex metal salts, has deduced the following theory of the mechanism of action of oxidases, peroxidases and catalases. According to him the oxidase combines loosely with H_2O in which process, part of its energy is transferred to H_2O and activate it to $HO-H$. The OH radical dehydrogenates the substrate molecule and H combines with atmospheric oxygen or with any other hydrogen acceptor. The peroxidase combines with hydrogen peroxide and similarly activates it to HO – OH. The HO radical dehydrogenates the substrate molecules. In a like manner, catalase activates H_2O_2 simultaneously to H – O – O – H and HO – OH. By mutual hydrogenation and dehydrogenation of these two activated forms, decomposition of hydrogen peroxide takes place. Thus the mechanism of the action of these enzymes is virtually the same. He showed that the mechanism of the activation of hydrogen peroxide by complex metal salts and by natural peroxidases was identical, since mutual interference occurs in solutions containing the complex metal salt together with the natural enzyme.

Now the study of the behaviour of peroxidases and tungstic acid, molybdic acid, vanadic acid with different substrates shows that the mechanism of reaction is not the same in both cases. Should the peroxidase activity be due to its combination with hydrogen peroxide alone as is the case with sols, there would not be such a marked difference as given in sections (B) and (C), when there is an increase in the concentration of reducing substrate and hydrogen peroxide, the products of reaction being the same in both cases. The difference may be due to the adsorption of both reducing substrate and hydrogen peroxide in the case of peroxidase as has been assumed by Mann (*loc. cit.*).

The author wishes to express his gratitude to Prof. J. C. Ghosh for interest and help during the progress of this work.

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REVIEWS

Text-book of Quantitative Inorganic Analysis. BY I. M. KOLTHOFF AND E. B. SANDELL. PUBLISHED BY THE MACMILLAN COMPANY, NEW YORK, 1936. PP 749. PRICE, $4.50.

Those, who have read the two volumes of "Volumetric Analysis" by Kolthoff, will surely look up with great expectation to the present work by the same author on "Quantitative Inorganic Analysis." This expectation is more than fulfilled by a single perusal of the book.

The most important feature of the book is its admirable and lucid treatment of the theoretical principles underlying the different analytical methods and procedures.

The book is divided mainly into four parts. In the first part, dealing with gravimetric analysis, a full and clear treatment of the fundamental theoretical principles of such analysis has been given. The chapters on "Formation and properties of precipitates" and " Co-precipitation phenomena" need special mention in this connection. The reviewer has seldom met with such an able exposition of these very important subjects in any other text-book of analytical chemistry. This is followed by an account of the practical technique of quantitative analysis, such as the use of balance, calibration of weights, etc. A chapter is also devoted on the discussion of errors in quantitative analysis. The first part closes after describing clearly in detail the procedures for the determination of certain important individual elements and for their separation from one another. The procedures for the complete analysis of a typical rock like lime-stone and an account of electrolytic determinations are included in this part.

The second part relates to volumetric analysis and follows the arrangement of the first part. A discussion of the theoretical principles involved in the various methods of volumetric analysis including those of electrometric titrations is followed by an account of the use of volumetric apparatus and the methods of their calibration. Finally, the methods of procedure for a number important volumetric determinations have been fully described.

The third part deals with the principles and procedures of the colorimetric and spectrophotometric methods.

Methods of procedures for the complete analysis of a few typical complex materials, such as brass, steel and silicate rocks, are described in the last part.

The authors have purposely avoided describing a large number of individual analytical procedures and have confined themselves only to a few typical examples which have been dealt with in all details, explanation, precision and care, so essential for the treatment of any analytical problem. A student, who has been able to make himself familiar with these examples described in the present volume, will find little difficulty in selecting the corresponding procedures for the analysis of any new material.

There are a few inaccurate or incomplete statements in the book; for instance, on p. 81, in describing the uses of quinaldinic acid as a reagent, the authors state that "copper can be quantitatively determined in the presence of these (Cd, Mn and Co) metals"; whereas this separation can be effected in the presence of many other substances such as Pb, Ni, P_2O_5, As_2O_3, As_2O_5, alkaline earths and magnesium. Similarly, it has not been mentioned that zinc can be estimated by quinaldinic acid in the presence of P_2O_5, Fe, Al, Be, U and Ti besides Mn, Mg, Ba, Ca etc.

Further, on p. 72, in dealing with precipitation at controlled p_H the authors give prominence to their own method based on the use of benzoic acid and ammonium benzoate. We have tried this method in our laboratory and found it of little use, specially in the separation of Cr from Co. The authors have summarily dismissed the hexamine methods, developed by the reviewer, which has been found quite useful by several workers in the separation of Fe from Zn, Mn, Ni and Co.

However, these are of minor importance.

There seems to be an error on p. 413, line 3 and 4 from the bottom, where the word "mole" should be substituted by "atom."

This book should be owned, read and used by all students of chemistry, to whom it may be strongly recommended. Even the teachers will find it of great help and use during the course of their instruction and work.

The printing and get-up of the book leave nothing to be desired, and the price is also moderate.

P. R.

Chemists, their Lives and Works. BY S. V. DIVEKAR, B.Sc. PUBLISHED BY THE STANDARD PUBLISHING COMPANY, BOMBAY, 1936. PP. 298 + XIV.

The lives and works of as many as thirtyone chemists (along with their portraits) have been embodied in this small volume and the author has been forced to condense the matter. This volume is specially intended for the B.Sc. students of the Bombay University and the author 'has always kept in mind two main facts, firstly to pick up as many chemists as possible and secondly to condense their works in such a way that facts are not sacrificed for space and time believing that the experimental details can be easily picked up by any one who desires to do so.'

The book is a welcome abridged edition of the voluminous books on this subject and would be very much helpful to the students as the salient features of the works of the distinguished chemists have been represented with precision and brevity. The inclusion of the works of some of the living chemists has made the book all the more attractive. The life and work of Sir P. C. Rāy, the father of chemical research in India and the founder of the Indian Chemical Society, would be a source of inspiration to the young generation of chemists.

In spite of the care taken by the author minor inaccuracies have crept into the book. The Author-Index, the Subject-Index and the Bibliography have added to the usefulness of the book, but a keen student will seriously miss the references to original Journals, which a book of this nature is expected to contain.

D. C.

THE INFLUENCE OF STRONG ELECTROLYTES AND MERCURIC CHLORIDE ON THE CONDUCTIVITY OF AQUEOUS BENZOIC ACID.

BY SHRIDHAR SARVOTTAM JOSHI AND DUSHYANT NARASINGASA SOLANKI.

Alfred Tingle (*J. Amer. Chem. Soc.*, 1899, **31**, 792) was perhaps the first to make accurate measurements of the electrical conductivity of benzoic acid in aqueous solutions The conductivity of such a weak acid in the presence of electrolytes has been studied by various investigators. Pouchon measured the conductivity of phosphoric acid in the presence of its salts (*Radium J.*, 1908, **5**, 167). Boeseken and Verkade (*Rec. trav. chim.*, 1916, **36**, 167) studied the influence of oxalic acid on the conductivity of aqueous boric acid. Kendall and Andrews (*J. Amer. Chem. Soc.*, 1921, **43**, 1545) from solubility measurements found that the solubility of benzoic acid is depressed due to HCl added, and that the conductivity of HCl is reduced by benzoic acid. McBain and Kam (*J. Chem. Soc.*, 1919, **115**, 1332) studied the effect of a number of neutral salts on a weak organic acid like acetic acid, by vapour pressure measurements. Kolthoff and Bosh (*Rec. trav. chim.*, 1927, **46**, 430) observed that these salts decrease the H-ion activity in dilute HCl solutions but at higher concentrations have the reverse effect. Meer Wien (*Annalen*, 1927, **455**, 227) observed an increase in the ionisation of weak electrolytes by complex formation. Kolthoff (*Rec. trav. chim* , 1928, **47**, 861, 872) showed that neutral saits increase the activity of undissociated acid; the constant *K* is not increased, in close agreement with the results obtained by Guntelberg and E. Schildt (*Z. physikal. Chem.*, 1928, **135**, 393). The influence of neutral salts on acids, with special reference to catalysis in solutions, has been discussed by Dawson (*Proc. Leeds Phil. Soc.*, 1929, **1**, 491). Larson (*Sveнsk. Kem Tidsks* , 1929, **41**, 130) has studied the effect of strong electrolytes on the distribution of acetic acid between water and an organic solvent like benzene, ether, etc. The activity coefficients of benzoic acid, the benzoate ion, in the presence of neutral salts, have been studied from E. M. F. and solubility measurements by various investigators.*

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* Chase and Kilpatrick (*J. Amer. Chem. Soc.*, 1931, **53**, 2589; 1931, **53**, 1732); Larson (*Z. physikal. Chem.*, 1931, **153**, 466; 1931, **153**, 299; *Z. anorg. Chem* , 1931, **196**, 354; *Z. physikal. Chem.*, 1931, **157**, 342); Kolthoff and Bosch (*J. Phys Chem.*, 1932, **36** 1685, 1695, 1702).

Recently a number of investigators† have determined the dissociation constant K of benzoic acid at 25° from conductivity and solubility measurements, which show K to be variable in the range $6{\cdot}295 \times 10^{-5}$ to $6{\cdot}7 \times 10^{-5}$. The value recorded in this paper is $6{\cdot}24 \times 10^{-5}$ (*cf.* Table I) which is very near the results of Saxton and Meir (*loc. cit.*). Data are given to show the influence of different concentrations of LiCl, NaCl KCl, RbCl, CsCl, HCl, $BaCl_2$ and $HgCl_2$ The inclusion of $HgCl_2$ was suggested by observation of some of its rather remarkable and anomalous behaviour as a coagulant (*cf.* Joshi and Kulkarni, *J. Indian Chem. Soc.*, 1936, **13**, 439; Joshi and Menon, *ibid.*, 1937, **14**, 103; Joshi and Ramdas, *ibid.*). It might also be added that some unpublished work by Mr. Haldhar and one of us from these laboratories showed a depression, in numerous cases, of the partition coefficient of benzoic acid between toluene and water in the presence of the electrolytes This might be due to (*a*) an increase in the ionisation of benzoic acid in the aqueous phase, (*b*) a "salting-out effect", (*c*) alteration of such factors as the solubility, dielectric constant and therefore the dissociating power of the medium. The addition of the electrolyte would also affect the degree of the polymerisation of the solvent (Subramann and Breyer, *Z. physikal. Chem*, 1933, **B**, **20**, 17, 53). It was of interest, therefore, to examine the above possibilities by studying the conductivity of aqueous benzoic acid in presence of the series of electrolytes mentioned above.

EXPERIMENTAL.

The conductivity determinations of benzoic acid in presence of the electrolytes—LiCl, NaCl, KCl, RbCl, CsCl, $BaCl_2$, HCl and $HgCl_2$ of Kahlbaum's guaranteed extra pure chemicals were made at 25 ± 0·1°. The containers were all of high resistance Jena glass. The conductivity cell, used, was of Pyrex glass; with the platinum electrodes, each of 1 sq. cm. area, fixed vertically, the inter-electrode distance being 1·2 cm. The bridge employed for the determination of electrolytic resistances was Pye's modified Post Office Box of dial resistance type; a small Kohlrausch's induction coil was used as an A.C. generator. The conductivity water used for experiments was prepared by distilling twice distilled water in a silica distiller and collecting only the middle fraction. This stock of water which was used for making the various solutions was examined every now and then for its constancy of conductivity, the specific conductivity being 1.878×10^{-6} mhos. The cell constant was determined every now and then by using freshly prepared $N/50$-KCl solution at 25 ± 0·1°. The electrodes with fresh platinised surfaces were always kept immersed in conductivity water after the completion of an experiment.

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† Brockmann and Kilpatrick (*J. Amer. Chem. Soc.*, 1934, **56**, 1483); Vogel and Jeffery (*Chem. Ind.*, 1934, **53**, 779, *Phil. Mag.*, 1934, *vii*, **18**, 901); Saxton and Meir (*J. Amer. Chem. Soc.*, 1934, **56**, 1918).

Table I gives the values for the conductivities of benzoic acid for different concentrations ($N/50$ to $N/1200$) For calculating the value of α, the degree of ionisation, the value for the equivalent conductivity (Λ_∞) of benzoic acid at infinite dilution is taken to be 381·3 mhos. The values for K, the dissociation constant, are recorded in the last column.

In Tables II to XXI are recorded the values for the conductivities of the mixture of benzoic acid and each of the electrolytes mentioned above. The strength of the mixture in terms of its components, benzoic acid and the electrolyte, is recorded in column 1; the concentrations of the components are expressed for the system *after mixing*. Columns 2 and 3 give respectively the resistance in ohms for the mixed solutions and that for varying concentrations of the electrolyte, measured for the corresponding concentrations of the electrolyte present in the mixture as shown in column 1. In column 4 are given the specific conductivities in mhos for the mixtures; in column 5 are given the specific conductivities for the corresponding concentrations of the electrolyte. In column 6 are given the values for the specific conductivity of benzoic acid obtained by subtracting the specific conductivity of the electrolyte (column 5) from that of the mixture as given in column 4. The specific conductivity of pure benzoic acid is given at the bottom of column 6 in Table II. This scheme has been followed in the subsequent tables.

Tables II – III show the influence of LiCl in the range $N/64$—$N/4096$ for $N/100$ and $N/200$-benzoic acid. Tables IV-VI refer to NaCl whose concentration was varied over the above range in the presence of $N/100$, $N/150$ and $N/200$ benzoic acid. Tables VII—IX refer to KCl, the concentrations of both benzoic acid and KCl being the same as in the previous case. Tables X—XIII refer in the same way to RbCl and CsCl. Tables XIV—XVI refer to the use of $BaCl_2$, XVII and XVIII of HCl and XIX—XXI to that of $HgCl_2$.

In drawing the curves, shown in Figs. 1, 2, 3, the square roots of the normalities of each of the above electrolytes (except in the case of $HgCl_2$, Fig. 3) have been plotted along the abscissæ; the corresponding specific conductivities of the benzoic acid in the mixture, as calculated by difference, are shown along the ordinates.

TABLE I.

Conductivities of benzoic acid soln. at 25 + 0·1°.

Strength of acid	Resistance.	Conductivity Sp.	Conductivity equiv	Degree of ionisation.	Dissoc. const. K.
N/50	899·0	0·0004154	20·77	0·05449	$6·28 \times 10^{-5}$
N/100	1279·0	0·0002913	29·13	0·07640	6·32
N/200	1853·0	0·0002011	40·22	0·1055	6·222
N/400	2695·0	0·0001382	55·28	0·1450	6·13
N/75	1107·0	0·0003367	25·25	0·06623	6·269
N/150	1594·0	0·0002337	35·06	0·09196	6·21
N/300	2306·0	0·0001616	48·48	0·1272	6·174
N/600	3329·0	0·0001120	67·16	0·1762	6·277
N/1200	4899·0	0·00007605	91·27	0·2394	6·279
				Mean	$6·24 \times 10^{-5}$

TABLE II.

Mixture of N/100-benzoic acid and LiCl at 25 ±0·1°.

No.	Composition. Benzoic acid	Composition. Lithium chloride	Resistance of mixture.	Resistance of LiCl only	Specific conductivity of mixture.	Specific conductivity of LiCl only.	Specific conductivity of N/100-benzoic acid calc. from diff.
1	N/100	N/64	195·3	232·6	0·001931	0·001622	0·0003090
2	,,	N/128	332·5	452·0	0·001116	0·0008332	0·0002828
3	,,	N/256	523	892·0	0·0007201	0·0004211	0·0002990
4	,,	N/512	736·5	1743·0	0·0005107	0·0002144	0·0002963
5	,,	N/1024	930·0	3418·5	0·0004041	0·0001082	0·0002949
6	,,	N/2048	1075·5	6680·0	0·0003491	0·00005424	0·0002949
7	,,	N/4096	1165	12850·0	0·0003221	0·00002709	0·0002951
8	,, only.						0·0002913

In the tables Resistance (R) has been expressed in ohms, and Conductivity (sp. and equiv.) in mhos.

TABLE III.

Mixture of N/200-benzoic acid and LiCl.

Cell constant = 0.3777.

No.	Composition.		R. of mixture.	Specific conductivity of mixture.	Specific conductivity of *N*/200-acid calc. from diff.
	Benzoic acid	Lithium chloride			
1	*N*/200	*N*/64	205·1	0·001839	0·0002173
2	,,	*N*/128	361·6	0·001042	0·0002090
3	,,	*N*/256	597·0	0·0006306	0·0002095
4	,,	*N*/512	896·0	0·0004195	0·0002051
5	,,	*N*/1024	1198·0	0·0003132	0·0002050
6	,,	*N*/2048	1456·0	0·0002574	0·0002032
7	,,	*N*/4096	1618·0	0·0002314	0·0002043
8	,, only				0·0002011

TABLE IV.

Mixture of N/100-benzoic acid and NaCl.

No.	Composition.		Resistance of mixture	Resistance of NaCl only.	Specific conductivity of mixture.	Specific conductivity of NaCl only.	Specific conductivity of *N*/100-acid calc. from diff.
	Benzoic acid	Sodium chloride					
1	*N*/100	*N*/64	177·4	205·6	0·002126	0·001835	0·0002910
2	,,	*N*/128	307·45	399·0	0·001226	0·0009446	0·0002816
3	,,	*N*/256	490·0	777·6	0·0007689	0·0004839	0·0002850
4	,,	*N*/512	703·4	1536·5	0·0005351	0.0002440	0·0002911
5	,,	*N*/1024	913·2	3004·0	0·0004117	0·0001239	0·0002878
6	,,	*N*/2048	1062·0	5895·0	0·0003538	0·00006223	0·0002916
7	,,	*N*/4096	1158·0	11200·0	0·0003243	0·00003189	0·0002924
8	,, only.						0·0002913

TABLE V.

Mixture of N/150-benzoic acid and NaCl

No.	Composition.		R. of mixture.	Specific conductivity of	
	Benzoic acid	Sodium chloride		mixture.	*N*/150-acid calc. from diff.
1	*N*/150	*N*/64	182·3	0·002070	0·0002350
2	,,	*N*/128	321·0	0·001171	0·0002266
3	,,	*N*/256	529·0	0·0007121	0·0002282
4	,,	*N*/512	755·4	0·0004790	0·0002350
5	,,	*N*/1024	1053·4	0·0003566	0·0002327
6	,,	*N*/2048	1268·0	0·0002960	0·0002358
7	,,	*N*/4096	1402·0	0·0002677	0·0002338
8	,, only.				0·0002337

TABLE VI.

Mixture of N/200-benzoic acid and NaCl.

No.	Composition		R. of mixture.	Specific conductivity of	
	Benzoic acid	Sodium chloride		mixture.	*N*/200-acid calc. from diff.
1	*N*/200	*N*/64	185·2	0·002037	0·0002020
2	,,	*N*/128	331·3	0·001136	0·0001936
3	,,	*N*/256	558·0	0·0006751	0·0001912
4	,,	*N*/512	845·5	0·0004448	0·0002008
5	,,	*N*/1024	1159·5	0·0003242	0·0002003
6	,,	*N*/2048	1420·0	0·0002642	0·0002037
7	,,	*N*/4096	1590·5	0·0002356	0·0002037
8	,, only.				0·0002011

TABLE VII.

Mixture of N/100-benzoic acid and KCl.

No.	Composition.		Resistance of		Specific conductivity of		
	Benzoic acid	Potassium chloride	mixture.	KCl.	mixture.	KCl only.	*N*/100-acid calc. from diff.
1	*N*/100	*N*/64	152·1	172·9	0·002481	0·002183	0·0002980
2	,,	*N*/128	268·0	337·2	0·001407	0·001118	0·0002890
3	,,	*N*/256	440·0	665·0	0·0008563	0·0005660	0·0002903
4	,,	*N*/512	653·2	1318·0	0·0005763	0·0002846	0·0002917
5	,,	*N*/1024	867·5	2604·0	0·0004334	0·0001431	0·0002903
6	,,	*N*/2048	1036·0	5114·0	0·0003627	0·00007198	0·0002907
7	,,	*N*/4096	1142·0	9825·0	0·0003288	0·00003656	0·0002923
8	*N*/100-acid only.						0·0002913

TABLE VIII.

Mixture of N/150-benzoic acid and KCl.

No.	Composition.		R. of mixture.	Specific conductivity of	
	Benzoic acid	Potassium chloride		mixture.	N/150-acid calc. from diff.
1	*N*/150	*N*/64	155·0	0·002434	0·0002510
2	,,	*N*/128	278·7	0·001353	0·0002350
3	,,	*N*/256	471·6	0·0007990	0·0002330
4	,,	*N*/512	727·0	0·0005176	0·0002330
5	,,	*N*/1024	996·0	0·0003772	0·0002341
6	,,	*N*/2048	1221·0	0·0003074	0·0002354
7	,,	*N*/4096	1378·0	0·0002721	0·0002356
8	*N*/150-acid only.	...	...	...	0·0002337

TABLE IX.

Mixture of N/200-benzoic acid and KCl.

No.	Composition.		R. of mixture	Specific conductivity of mixture	Specific conductivity of *N*/200-acid calc. from diff.
	Benzoic acid	Potassium chloride			
1	*N*/200	*N*/64	158·8	0·002376	0·0001930
2	,,	*N*/128	289·0	0·001305	0·0001870
3	,,	*N*/256	493·0	0·0007642	0·0001982
4	,,	*N*/512	778·0	0·0004835	0·0001989
5	,,	*N*/1024	1091·0	0·0003442	0·0002011
6	,,	*N*/2048	1370·0	0·0002738	0·0002018
7	,,	*N*/4096	1578·0	0·0002371	0·0002006
8	*N*/200 acid only.	...	...	.	0·0002011

TABLE X.

Mixture of N/100-benzoic acid and RbCl.

No.	Composition.		Resistance of mixture	Resistance of RbCl only	Specific conductivity of mixture	Specific conductivity of RbCl only	Specific conductivity of *N*/100-acid calc. from diff.
	Benzoic acid	Rubidium chloride					
1	*N*/100	*N*/128	260·4	326·2	0·001448	0·0001156	0·0002920
2	,,	*N*/256	428·6	647·4	0·0008794	0·0005815	0·0002979
3	,,	*N*/512	635·5	1278·0	0·0005925	0·0002937	0·0002988
4	,,	*N*/1024	847·8	2490·0	0·0004436	0·0001499	0·0002937
5	,,	*N*/2048	1022·0	4948·0	0·0003678	0·00007450	0·0002933
6	,,	*N*/4096	1136·0	9627·0	0·0003307	0·00003740	0·0002933
7	*N*/100-acid only.		...	...	...	...	0·0002913

TABLE XI.

Mixture of N/200-benzoic acid and RbCl.

No.	Composition.				Resistance of mixture.	Specific mixture.	conductivity of *N*/200-acid calc. from diff.
1		*N*/200		*N*/128	277·2	0·001361	0·0002045
2	Ben oic acid	,,	Rubidium chloride	*N*/256	477·9	0·0007885	0·0002070
3		,,		*N*/512	751·0	0·0005011	0·0002074
4		,,		*N*/1024	1063·0	0·0003535	0·0002036
5		,,		*N*/2048	1354·0	0·0002771	0·0002026
6		,,		*N*/4096	1565·0	0·0002395	0·0002021
7		*N*/200a-cid only.		...	...	...	0·0002011

TABLE XII.

Mixture of N/100-benzoic acid and CsCl.

No.	Composition				Resistance of mixture,	Resistance of CsCl only.	Specific conductivity of mixture.	Specific conductivity of CsCl.	Specific conductivity of *N*/100-acid calc. from diff.
1		*N*/100		*N*/128	261·2	325·5	0·001445	0·001158	0·0002870
2	Benzoic acid	,,	Caesium chloride	*N*/256	425·4	645·4	0·0008860	0·0005832	0·0003025
3		,,		*N*/512	638·3	1275·0	0·0005899	0·0002941	0·0002955
4		,,		*N*/1024	850·5	2488·5	0·0004422	0·0001499	0·0002923
5		,,		*N*/2048	1019·0	4945·0	0·0003690	0·00007456	0·0002944
6		,,		*N*/4096	1131·0	9648·0	0·0003321	0·00003731	0·0002948
7		*N*/100-acid only.			...	...	...	...	0·0002913

TABLE XIII.

Mixture of N/200-benzoic acid and CsCl.

No.	Composition.		Resistance of mixture.	Specific conductivity of mixture.	Specific conductivity of N/200-acid calc. from diff
	Benzoic acid	Caesium chloride			
1	*N*/200	*N*/128	276·3	0·001365	0·0002070
2	,,	*N*/256	475·5	0·0007923	0·0002091
3	,,	*N*/512	752·5	0·0005001	0·0002057
4	,,	*N*/1024	1061·5	0·0003540	0·0002041
5	,,	*N*/2048	1348·0	0·0002783	0·0002037
6	,,	*N* 4096	1553·5	0·0002413	0·0002040
7	*N*/200-acid only.	. .	..	..	0·0002011

TABLE XIV.

Mixture of N/100-benzoic acid and BaCl$_2$.

No,	Composition.		Resistance of mixture.	Resistance of BaCl$_2$ only.	Specific conductivity of mixture	Specific conductivity of BaCl$_2$ only.	Specific conductivity of N 100-acid calc.from diff.
	Benzoic acid	Barium chloride					
1	N/100	*N*/64	170·0	197·5	0·002220	0·001910	0·0003100
2	,,	*N*/128	292·0	380·8	0·001291	0·0009898	0·0003013
3	,,	*N*/256	465·5	740·0	0·0008093	0·0005085	0·0003012
4	,,	*N*/512	675·0	1452·0	0·0005571	0·0002582	0·0002989
5	,,	*N* 1024	881·5	2824·5	0·0004266	0·0001319	0·0002947
6	,,	*N*/2048	1043·0	5468·5	0·0003602	0·00006719	0·0002930
	N/100-acid only.		.	...	...	...	0·0002913

TABLE XV.

Mixture of N/150-benzoic acid and $BaCl_2$.

No.	Composition		R of mixture	Specific conductivity of	
	Benzoic acid	Barium chloride		mixture.	N/150-acid calc. from diff.
1	N/150	N/64	176·8	0·002134	0·0002240
2	„	N/128	309·9	0·001216	0·0002263
3	„	N/256	508·9	0·0007401	0·0002316
4	„	N/512	750·0	0·0005016	0·0002432
5	„	N/1024	1028·0	0·0003656	0·0002337
6	„	N/2048	1247·0	0·0003010	0·0002338
7	N/150-acid only.		...	...	0·0002337

TABLE XVI.

Mixture of N/200-benzoic acid and $BaCl_2$.

No.	Composition.		R. of mixture.	Specific conductivity of	
	Benzoic acid	Barium chloride		mixture.	N/200-acid calc. from diff.
1	N/200	N/64	177·5	0·002125	0·0002150
2	„	N/128	318·0	0·001186	0·0001963
3	„	N/256	526·0	0·0007169	0·0002084
4	„	N/512	809·0	0·0004650	0·0002068
5	„	N/1024	1109·0	0·0003387	0·0002068
6	„	N/2048	1393·0	0·0002692	0·0002020
7	N/200-acid only		...	..	0·0002011

TABLE XVII.

Mixture of N/100-benzoic acid and HCl.

No	Composition.		Resistance of mixture	Resistance of HCl only	Specific conductivity of mixture	Specific conductivity of HCl only.	Specific conductivity of *N*/100-acid calc. from diff.
	Benzoic acid	Hydrochloric acid					
1	N/100	*N*/64	58·3	58·5	0·006475	0·006453	0·00002200
2	,,	*N*/128	114·0	115·2	0·003311	0·003276	0·00003500
3	,,	*N*/256	221·1	228·2	0·001707	0·001653	0·00005350
4	,,	*N*/512	406·6	456·6	0·0009272	0·0008252	0·0001020
5	,,	*N*/1024	650·5	908·0	0·0005789	0·0004141	0·0001648
6	,,	*N*/2048	883.0	1819·0	0·0004255	0·0002058	0·0002197
7	,,	*N*/4096	1050·0	3698·0	0·0003578	0·0001010	0·0002568
8	*N*/100-acid only.		...	...	...	...	0·0002913

TABLE XVIII.

Mixture of N/200-benzoic acid and HCl.

No	Composition.		R of mixture.	Specific conductivity of mixture.	Specific conductivity of *N*/200-acid calc. from diff.
	Benzoic acid	Hydrochloric acid			
1	N/200	*N*/64	58·8	0·006421	−0·00003200
2	,,	*N*/128	115·0	0·003282	+ 0·000006000
3	,,	*N*/256	228·0	0·001655	+ 0·000001500
4	,,	*N*/512	432·6	0·0008712	+ 0·000004600
5	,,	*N*/1024	742·8	0·0005065	0·00009238
6	,,	*N*/2048	1162·5	0·0003408	0·0001350
7	,,	*N*/4096	1408·0	0·0002665	0·0001655
8	*N*/200-acid only.		...	...	0·0002011

TABLE XIX.

Mixture of N/100-benzoic acid and $HgCl_2$.

No.	Composition.		R. of mixture	Specific conductivity of		
	Benzoic acid	Mercuric chloride		mixture.	$HgCl_2$ only.	N/100-acid calc. from diff
1	N/100	0·25 N	819·8	0·0004586	0·0001640	0·0002937
2	,,	0·1875	880·3	0·0004271	0·0001370	0·0002892
3	,,	0·1406	932·0	0·0004032	0·0001101	0·0002841
4	,,	0·1054	980·0	0·0003834	0·0001021	0·0002813
5	,,	0·07911	1018·0	0·0003692	0·00008873	0·0002805
6	,,	0·05933	1056·0	0·0003558	0·00007736	0·0002785
7	,,	0·0445	1093·0	0·0003437	0·00006847	0·0002753
8	,,	0·03338	1119·0	0·0003358	0·00006060	0·0002752
9	,,	0·02503	1139·0	0·0003290	0·00005353	0·0002764
10	,,	0·01878	1611·0	0·0003235	0·00004761	0·0002759
11	N/100-acid only.		...	...	...	0·0002913

TABLE XX.

Mixture of N/150-benzoic acid and $HgCl_2$.

No.	Composition		R. of mixture.	Specific conductivity of	
	Benzoic acid	Mercuric chloride		mixture.	N/150-acid calc. from diff.
1	N/150	0·25 N	955·0	0·0003936	0·0002287
2	,,	0·1875	1038·0	0·0003621	0·0002242
3	,,	0·1406	1104·1	0·0003403	0·0002212
4	,,	0·1054	1174·5	0·0003199	0·0002178
5	,,	0·07911	1222·0	0·0003073	0·0002186
6	,,	0·05933	1268·0	0·0002961	0·0002188
7	,,	0·04450	1318·5	0·0002849	0·0002165
8	,,	0·03338	1352·0	0·0002777	0·0002171
9	,,	0·02503	1375·0	0·0002730	0·0002195
10	,,	0·01878	1413·5	0·0002656	0·0002180
21	N/150-acid only.		...	...	0·0002337

TABLE XXI.

Mixture of N/200-benzoic acid and $HgCl_2$.

No	Composition.		R of mixture	Specific conductivity of	
	Benzoic acid	Mercuric chloride		mixture	N/200-acid calc. from diff.
1	N/200	0·25 N	1075·0	0·0003494	0·0001845
2	,,	0·1875	1160·0	0·0003238	0·0001859
3	,,	0·1406	1252·0	0·0002999	0·0001808
4	,,	0·1054	1316·0	0·0002855	0·0001834
5	,,	0·07911	1385·0	0·0002709	0·0001822
6	,,	0·05933	1448·0	0·0002592	0·0001819
7	,,	0·04450	1497·0	0·0002507	0·0001823
8	,,	0·03338	1551·0	0·0002420	0·0001814
9	,,	0·02503	1600·0	0·0002345	0·0001810
10	,,	0·01878	1631·0	0·0002300	0·0001824
11	N/200-acid only.		...	...	0·0002011

TABLE XXII.

Mixture of N/100-benzoic acid after mixing at 25 ± 0·1°.

Conc. of HCl in the mixture	Degree of ionisation for N/100-benz. acid in presence of HCl.	Reduced sp. conduct of N/100-benz. acid.	Sp. Conductv. of N/100-benz. acid calc. from diff.
C.	α.		
N/64	0·00410	0·0000156	0·0000220
N/128	0·00798	0·0000304	0·0000350
N/256	0·0153	0·0000583	0·0000535
N/512	0·0275	0·000105	0·000102
N/1024	0·0429	0·000163	0·000165
N/2048	0·0565	0·000215	0·000220
N/4096	0.0655	0·000250	0·000257
0	0·0764	1·000291	0·000291

TABLE XXIII.

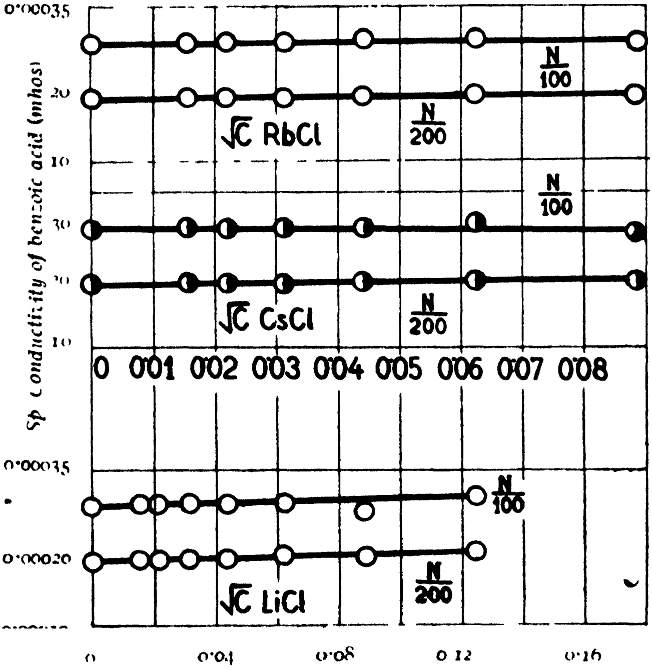
Temperature = 25 ± 0·1°.

1	2	3	For N/100-Benzoic acid 4	5	6	For N/150-Benzoic acid. 4′	5′	6′	For N/200-Benzoic acid. 4″	5″	6″
Conc. of $HgCl_2$ in mixture.	% Hydrolysis for $HgCl_2$.	Conc. of H^+ in g. equiv per litre C.	Degree of Ionisation in presence of $HgCl_2$ α.	Reduced sp. conducty. in mhos.	Sp. conduct. calc. from diff in mhos.	Degree of ionisation in presence of $HgCl_2$. α′.	Reduced sp. conduct. in mhos.	Sp. conduct. calc. from diff. in mhos.	Degree of ionisation in presence of $HgCl_2$. α″.	Reduced sp. conduct. in mhos.	Sp. conduct. calc from diff. in mhos.
0·25 N	0·12 %	0·00030	0·0633	0·000241	0·000294	0·0738	0·000188	0·000229	0·0817	0·000156	0·000185
0·1875	0·14	0·000263	0·0648	0·000247	0·000289	0·0758	0·000193	0·000224	0·0844	0·000161	0·000186
0·1406	0·17	·0·000239	0·0657	0·000250	0·000284	0·0772	0·000196	0·000221	0·0861	0·000164	0·000181
0·1054	0·20	0·000211	0·0669	0·000254	0·000281	0·0788	0·00020	0·000218	0·0882	0·000168	0·000183
0·07911	0·23	0·000182	0·0681	0·000259	0·000280	0·0805	0·000205	0·000219	0·0904	0·000172	0·000182
0·05933	0·27	0·000158	0·0691	0·000263	0·000279	0·0821	0·000209	0·000219	0·0924	0·000176	0·000182
0·0445	0·31	0·000138	0·070	0·000267	0·000275	0·0833	0·000212	0·000217	0.0940	0.000179	0·000182
0·03338	0·37	0·000124	0·0706	0·000269	0·000275	0·0842	0·000214	0·000217	0·0953	0·000182	0·000181
0·02503	0·43	0·000108	0·0713	0·000272	0·000276	0·0853	0·000217	0·000219	0·0965	0·000184	0·000181
0·01878	0·51	0·0000958	0·0718	0.000274	0·000276	0·0861	0.000219	0·000218	0·0975	0·000186	0·000183
0	...	...	0·0764	0·000291	0·000291	0·0920	0·000234	0·000234	0·106	0·000201	0·000201

DISCUSSION.

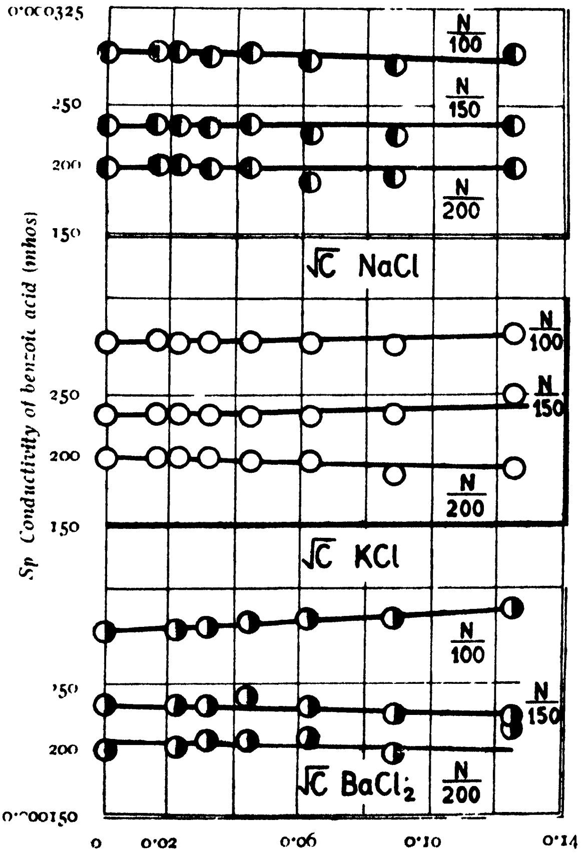
These results for the conductivity of aqueous benzoic acid in the presence of LiCl, NaCl, KCl, RbCl, CsCl, $BaCl_2$, HCl and $HgCl_2$, in their various concentrations, show, that except in the case of the last two substances (*cf.* Tables XVII—XXI, Fig. 3), the additive law holds; the specific conductivity of the mixture equals the sum of the specific conductivities of the two components, each determined separately. The absence of any alteration in the specific conductivity of a weak acid like benzoic acid in the presence of the above salts (except $HgCl_2$) even at low concentration (*cf.* Tables II—XVI, last column) as shown by the almost horizontalness of specific conductivity—$\sqrt{}$concentration curves in Figs. 1 and 2 is interesting. The results of numerous investigators on " the neutral salt effect ", which is ordinarily shown rather markedly by weak acids suggests an increase in H^+ concentration or rather, in H^+ ion activity and therefore in the corresponding dissociation constant. McBain and Kam (*loc. cit.*) find evidence to the contrary.

FIG. 1.



They argue that the electrical potential of a hydrogen electrode is determined by the product of the chemical potential and $H^{\cdot}$ ion concentration, *i.e.*, its *activity*. The experimental fact, *viz.*, that the potential of a hydrogen electrode is increased in an aqueous solution of a weak acid in the presence of a neutral salt indicates an increase in $H^{\cdot}$ ion activity. McBain and Kam (*loc. cit.*) make an interesting postulate, *viz.*, that concommitantly with the last quantity, the activity of the undissociated molecules in the system is increased They adduced the experimental support for this in the

FIG. 2.



observation that the vapour pressure of acetic acid and therefore its activity is actually increased by the presence of a neutral salt like NaCl. The mass law expression in terms of the various activities for the ionisation equilibrium of such a weak acid in the presence of a neutral salt should therefore be unaltered, since the activities of both the undissociated acid and H^+ are affected equally. This leads to the result that the corresponding degree of dissociation and therefore the specific conductivity of the above acid would remain unaltered, despite the presence of the neutral salts. Our results on benzoic acid (Tables II-XVI, Figs. 1, 2) are in agreement with this deduction. The work of Chase and Kilpatrick (*loc. cit.*), Larson (*loc. cit.*) and Kolthoff and Bosch (*loc. cit.*) on the activity measurements of benzoic acid in the presence of the neutral salts (whose concentration was varied over a wide range) by E. M. F. and solubility methods has shown that the activity of undissociated benzoic acid molecules increases remarkably by the above additions.

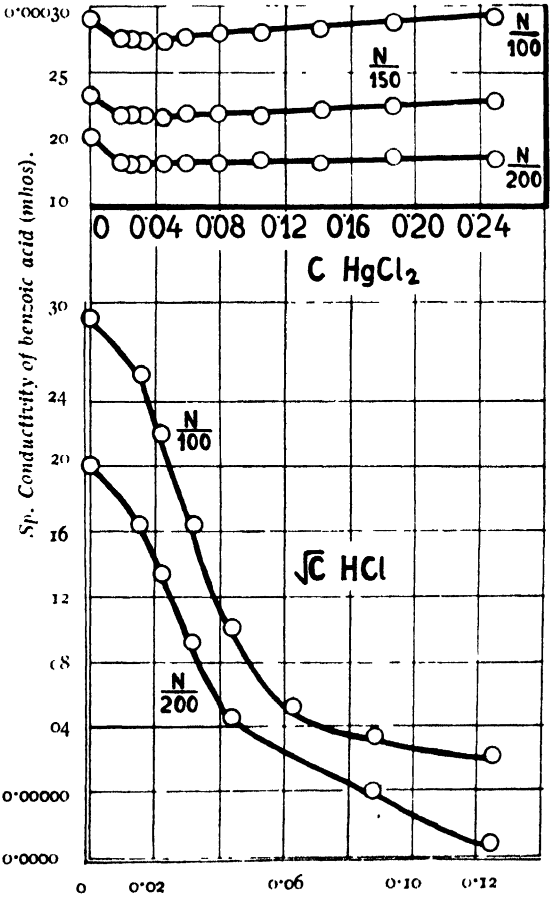
The results for the specific conductivity of benzoic acid at $N/100$ and $N/200$ in the presence of hydrochloric acid in the range $N/64$ to $N/4096$ show that the above quantity is diminished in the presence of the latter. That this can be ascribed to a substantial extent to the common ion effect is shown by the results in Table XXII. Assuming that for any of the values of C, the concentration of hydrochloric acid employed, α' its degree of ionisation is unity, α, the corresponding degree of dissociation for benzoic acid in its presence is given by the equation

$$\left(C\alpha' + \frac{\alpha}{V}\right).\,\alpha = K(1-\alpha),$$

where K is the dissociation constant of benzoic acid. These calculated values for α corresponding to various values of C for $N/100$-benzoic acid are shown in the 2nd vertical column in Table XXII. From a knowledge of α, Λ_∞, and the dilution for benzoic acid, the reduced specific conductivity for benzoic acid can be calculated. These values are also shown in the above table. Its last column gives the corresponding experimentally found values for benzoic acid in the presence of hydrochloric acid. Comparison of the last two columns shows that the agreement between the calculated and observed values is satisfactory. Similar results were obtained for $N/200$ benzoic acid.

Results on the influence of $HgCl_2$ given in Tables XIX-XXI show that the specific conductivity of benzoic acid is diminished in its presence. This dimunition at a given concentration of benzoic acid is sensible only at large dilutions of $HgCl_2$. Now it is known that $HgCl_2$ is hydrolysed, thus giving free HCl in aqueous solutions. Ley (*Z. physikal. Chem.*, 1899, **30**, 240) has given data for the degree of hydrolysis of $HgCl_2$ in the range N/16 to N/256; from these the degrees of hydrolysis for the dilutions used in this work were obtained by extrapolation and are shown in the 2nd column in Table XXIII, on the assumption that the degree of hydrolysis approaches zero as dilution tends to zero, which is substantially correct. From the data of Luther (*J. Phys. Chem.*, 1929, **33**, 943) for example, for the proportions of the various

Fig. 3.



molecular and ionic species in 0·26 M-$HgCl_2$ at 25°, the H^+ ion concentration seems to be negligibly small. The H^+ ion concentrations at these various dilutions are shown in the 3rd column, α, the degree of dissociation of benzoic acid in the presence of these H^+ being calculated from the above equation. In the same way the corresponding reduced (*i.e.* corrected for hydrolysis) specific conductivity of $N/100$- benzoic acid was calculated. These two quantities are shown in the 4th and 5th columns ; 6th column gives the actual value in the mixture *obtained by difference*. Similar calculations were made for $N/150$- and $N/200$-benzoic acid; columns $4'$, $5'$, $6'$ and $4''$, $5''$, $6''$ refer to them respectively, in Table XXIII. An examination of the results under columns 5, 6; $5'$, $6'$; $5''$, $6''$ shows clearly that the common ion effect arising out of the hydrolysis of $HgCl_2$, is one factor leading to a dimunition in specific conductivity of benzoic acid. On this basis, it is to be anticipated that in strong solutions of $HgCl_2$ corresponding to minimum hydrolysis, the common ion effect would be a minimum; it follows, therefore, that the specific conductivity of benzoic acid, obtained by difference would approach that of aqueous benzoic acid in the absence of a disturbing electrolyte. An examination of the results under the above columns show that the above deduction is in accord with the facts.

The results for the specific conductivity corrected for hydrolysis depart from those obtained by difference or by the additive law in the case of strong solutions of $HgCl_2$. This discrepancy might arise, possibly from the fact that extrapolation made on the assumption, *viz.*, negligibility of hydrolysis at very high concentrations, is not rigorously accurate, *i.e.*, it indicates more hydrolysis than what obtains under the conditions.

It might now be pointed out that in the above discussion of the results, a tacit assumption has been made that a weak acid like the benzoic would not affect the conductivity due to any of these substances examined in this work, *i.e.*, would not influence the molecular or the ionic reactivity characteristic of each of the added materials. In the case of $HgCl_2$, however, it would appear that this is not strictly true, which agrees with the fact that $HgCl_2$ stands apart from the rest of the substances examined in having some of the properties of a *weak electrolyte*. It is appreciably likely that this hydrolysis is sensibly suppressed by the presence of benzoic acid. Simms (*J. Phys. Chem.*, 1929, **33**, 745) has shown some evidence for the possible inactivation of a weak electrolyte in the presence of another. Sufficient data are not available in the literature for deducing such an effect from the current theories for the activity of a "weakly" ionised material. That the above possibility in the case of the hydrolysis of $HgCl_2$ is in agreement with experimental facts is suggested by an examination of data in Table XXIII. It is seen that the divergence from the specific conductivity of benzoic acid deduced from the additive law, of its conductivity, when corrected for hydrolysis of $HgCl_2$ is greater, the greater the concentration of benzoic acid, which suggests that since the extrapolation is a common factor, the above hydrolysis is affected (suppressed) by benzoic acid.

SUMMARY.

1. The mean value obtained for the dissociation constant of benzoic acid at 25° is $6{\cdot}24 \times 10^{-5}$, in close agreement with the recent values.

2. The specific conductivity of aqueous benzoic acid, whose concentration was varied in the range $N/100-N/200$, in the presence of the electrolytes—LiCl, NaCl, KCl, RbCl, CsCl, $BaCl_2$, HCl and $HgCl_2$, whose concentration was varied in the range $N/64-N/4096$, was determined, at 25°.

3. The additive law for the specific conductivity of the mixture of benzoic acid and electrolyte holds good especially in dilute solutions, except in the case of HCl and $HgCl_2$, where the specific conductivity is less than that given by the additive law. This has been ascribed to the common ion effect in the former and due to hydrolysis of the latter.

4. Evidence is also adduced to show a possible suppression on the hydrolysis of $HgCl_2$ by the benzoic acid.

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SOME BASES OF PHYSIOLOGICAL INTEREST.

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At one time, it seemed probable that chaksine iodide, an alkaloid isolated from *Cassia absus* by Siddiqui and Ahmed (*Proc. Indian Acad. Sci.*, 1935, **5**, 421) had the structure represented by (I). It was thought of interest to synthesise the substance.

$$\underset{\text{(I)}}{Ph{\cdot}CH(OH){\cdot}CH_2{\cdot}NH{\cdot}C{:}(NH){\cdot}NMe_3I} \qquad \underset{\text{(II)}}{Ph{\cdot}CH(OH){\cdot}CH_2{\cdot}NH{\cdot}C({:}NH){\cdot}NH_2}$$

It was expected that β-hydroxy-β-phenylethyldimethylguanidine would add methyl iodide to give (I). Schotte, Priewe and Roescheisen (*Z. physiol. Chem.*, 1928, **174**, 119) have prepared phenyldiethylguanidine by condensing diethyl cyanamide and aniline hydrochloride in a sealed tube for 20 hours. But dimethyl cyanamide did not give the corresponding guanidine with β-hydroxyphenylethylamine* although no difficulty was experienced in condensing it with aniline at ordinary pressure. Phenyldimethylguanidine readily gave a quaternary iodide with methyl iodide

By the interaction of β-hydroxy-β-phenylethylamine and methyl-ψ-thiourea hydroiodide, the hydroiodide of guanidine (II) was readily obtained in good yield. But the conversion of (II) into (I) has not yet succeeded.

As it became apparent that the structure of chaksine is perhaps more complicated than was supposed at first, this line of investigation was not further stressed at this stage In the present paper a description is included of some amines of physiological interest.

β-Hydroxy-β-phenylethylmethylamine has been prepared in good yield by the hydrolysis of the methyl iodide addition product of the Schiff's base of β-hydroxy-β-phenylethylamine and piperonal. Similarly, β-hydroxy-β-3:4-methylenedioxyphenylethylmethylamine (methylenedioxyadrenaline, III) has been prepared in an analogous way. This latter substance has been prepared by Barger and Jowett (*J. Chem. Soc.*, 1905, **87**, 970) from 3:4-methylenedioxyphenylethylene and the properties of this substance agree with those obtained in the present investigation. β-Hydroxy-β-phenylethyl trimethylammonium iodide (IV, β-phenylcholine iodide) and the corresponding 3′:4′-methylenedioxy derivative have also been synthesised.

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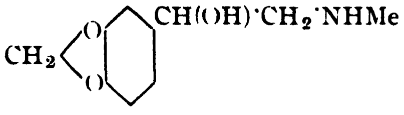
* This experiment was done under ordinary conditions. It is intended to carry out the reaction under pressure.



(III)

$Ph\cdot CH(OH)\cdot CH_2\cdot NMe_3I$.

(IV)

EXPERIMENTA

Phenyldimethylguanidine.—A mixture of dimethyl cyanamide (0·5 g.) and aniline hydrochloride (1 g.) was heated at 110-120° for 2 hours. The product was dissolved in water and extracted with ether. The aqueous layer was basified and then extracted with ether. After removal of the solvent, the syrup crystallised in *vacuo* after two days. It was recrystallised from petrol ether and ether in colourless needles, m.p. 90°. (Found: N, 25·2. $C_9H_{13}N_3$ requires N, 25·7 per cent). The substance combines with atmospheric carbon dioxide readily and is difficult to obtain analytically pure.

Phenyldimethylguanidinium Iodide, m.p. 188° (decomp.) after crystallisation from acetone and ether, was obtained when a mixture of the foregoing guanidine (0·4 g.) and methyl iodide (2 c.c.) in dry benzene (5 c.c.) was left overnight. (Found: N, 13·5. $C_{10}H_{16}N_3I$ requires N, 13·7 per cent).

β-Hydroxyphenylethylamine could not be prepared very satisfactorily by the method of Wolfheim (*Ber.*, 1914, **47**, 1444). But the following modification worked better :

Benzaldehyde cyanhydrin (16 g.) dissolved in 30% alcohol (250 c.c.) was cooled to − 10° and reduced with 500 g. of sodium amalgam (4%). The solution was kept neutral as far as possible by the addition of requisite quantities of 50% acetic acid from time to time. The addition of the amalgam was so regulated that the addition of the whole quantity required about 5 hours. The reaction was carried in a stout stoppered bottle. The temperature of the solution was never allowed to rise above −5°. The solution was then filtered from a green flocculent impurity and the clear filtrate acidified with hydrochloric acid and evaporated down to 50 c. c. and extracted repeatedly with ether (100 c.c.). The acidic aqueous portion was basified with 40% sodium hydroxide solution. During neutralisation the temperature should not rise above 10°. The base was extracted with ether (150 c.c.), the ethereal solution dried over potassium carbonate and slightly moist carbon dioxide passed into the ethereal solution, when the carbonate of the base was precipitated, m.p. 111-13°, yield 4-5 g. The dried carbonate (1 g.) was suspended in dry ether and treated with an ethereal solution of hydrogen chloride. After removal of ether in *vacuo*, the hydrochloride of β-hydroxyphenylethylamine (0·8 g.) crystallised from a mixture of ether and alcohol, m.p. 195°. (Found: N, 7·68 $C_8H_{12}ON$, HCl requires N, 8·0 per cent).

A solution of β-hydroxyphenylethylamine carbonate (0·2 g.) in hot alcohol was treated with picronolic acid (0.4 g.) dissolved in alcohol and cooled. The *picronolate*, m.p. 198 (decomp.) crystallised in fine yellow needles from alcohol. (Found : N, 17·44. $C_{18}H_{19}O_6N_5$ requires N, 17·45 per cent). The *oxalate*, m.p. 171-72°, crystallised in thin leaflets from alcohol. [Found: N, 7·60. $(C_8H_{11}NO)_2{\cdot}C_2H_2O_4$ requires N, 7·69 per cent].

The *monobenzoyl* derivative of β-hydroxyphenylethylamine is formed by benzoylating β-hydroxyphenylethylamine carbonate with excess of benzoyl chloride and sodium hydroxide solution. It crystallised from alcohol in fine needles, m p. 146 47°. (Found: N, 6·14. $C_{15}H_{15}O_2N$ requires N, 5·8 per cent). We are able to confirm the statement (*cf. Ber.*, 1914, **47**, 1445) that it is a *N*-benzoyl derivative *N O*-dibenzoyl-β-hydroxyphenylethylamine can be prepared in pyridine solution by the usual method. It crystallises from hot alcohol in colourless needles, m.p. 131-32°. (Found : N, 4·15. $C_{22}H_{19}O_3N$ requires N, 4·06 per cent).

Methiodide of β-Hydroxyphenylethylamine (IV).—A mixture of β-hydroxyphenylethylamine (1 g.), methyl iodide (4 c.c.) in dry benzene doposited the methiodide after standing for 12 hours It was collected, washed with dry ether and crystallised from hot alcohol in fine needles, m.p. 222°. (Found : N, 4·3 ; I, 42·0. $C_{11}H_{18}ONI$ requires N, 4·54 ; I, 41·3 per cent).

β-Hydroxyphenylethylamine did not condense with dimethyl cyanamide under varying conditions of experiment.

Piperonylidine-β-hydroxyphenylethylamine, m.p. 105-106 after crystallisation from alcohol, was prepared by condensing the base with piperonal in boiling alcohol in presence of caustic soda solution. (Found : N, 5·20. $C_{16}H_{15}O_3N$ requires N, 5·24 per cent).

β-Hydroxy-β phenylethylmethylamine—The foregoing Schiff's base (3 g.) dissolved in dry benzene (60 c.c.) was treated with methyl iodide (5 c.c.) and left for 2 days and then refluxed for 1 hour. The methyl iodide addition product separated as a sticky solid. This was dissolved in hot water and treated with hydrochloric acid and warmed for an hour. After cooling, the solution was extracted with ether to remove piperonal formed by hydrolysis and the aqueous portion made alkaline and the base extracted with ether. The ethereal solution furnished a solid which was directly converted into the picronolate as brilliant yellow needles, m.p. 196-98° after crystallisation from hot alcohol. (Found: C, 55·1; H, 5·2; N, 16·93. $C_{19}N_{21}O_6N_5$ requires C, 54·9; H, 5·0; N, 16·87 per cent).

Cyanhydrin of Piperonal.—The following method gives a good yield of the cyanhydrin of piperonal To a solution of piperonal (20 g.) in hot alcohol (20 c.c.) a solution of sodium hydrogen sulphite (30 g. in 50 c.c. of water) was added with shaking. The bisulphite compound was collected after cooling and washed with ether. The bisulphite compound suspended in water (*ca* 20 c c.) was shaken with a solution of potassium cyanide (20 g.) in water (20 c.c.) in the cold. The resulting cyanhydrin was extracted with ether, yield 16-18 g.

β-3′:4′-Methylenedioxyphenylethylamine.—Piperonal cyanhydrin (16 g) in 50% alcohol (220 c.c.) was reduced with sodium amalgam (500 g. of 4%) and the product isolated essentially as described under β-hydroxy-β-phenylethylamine except that chloroform was used for the extraction of the free base. The base was converted into the carbonate (yield 3-4 g.) in chloroform solution, m.p. 116-19° (decomp.). The hydrochloride crystallises from hot alcohol, m.p. 182-83°. (Found: N, 6·38; Cl, 16·7. $C_9H_{12}O_3NCl$ requires N, 6·45; Cl, 16·3 per cent). The *picronolate* crystallises in fine yellow needles, m.p 200° (decomp.). (Found: N, 15·47. $C_{19}H_{19}O_8N_5$ requires N, 15·75 per cent). The *oxalate* crystallises in plates, m p. 197°. (Found: N, 4·78. $C_{11}H_{13}O_7N$ requires N, 5·1 per cent). The carbonate was benzoylated with benzoyl chloride and aqueous alkali. The mono-*N*-benzoyl derivative crystallises from hot alcohol in fine needles, m.p. 152-53°. (Found: N, 5·05. $C_{16}H_{15}O_4N$ requires N, 4·91 per cent). The *O*-*N*-dibenzoyl derivative is formed in pyridine solution and crystallises from alcohol in colourless needles, m.p. 141-42°. (Found: N, 4·5. $C_{23}H_{19}O_5N$ requires N, 4·1 per cent).

β-3′:4′-Methylenedioxyphenylethyl trimethylammonium Iodide (structure analogous to IV).—The *base* described above (2 g.) was treated with methyl iodide (4 c.c.) in benzene. The methiodide crystallises from hot alcohol in needles, m.p. 229-30°. (Found: C, 40·8; H, 5·3; N, 4·46. $C_{12}H_{18}O_3NI$ requires C, 41·0; H, 5·1; N, 4·0 per cent).

Piperonylidine-β-hydroxy-β-3′:4′-methylenedioxyphenylethylamine.—The Schiff's base was prepared in alcoholic solution in presence of alkali and had m.p. 155-56° after crystallisation from alcohol. (Found: N, 4·26. $C_{18}H_{19}O_5N$ requires N, 4·28 per cent).

The foregoing Schiff's base (2·7 g.), dissolved in dry benzene (100 c.c.), was refluxed with methyl iodide (5 c.c.) for 2 hours. On standing a semi-solid mass separated, which was dissolved in water and hydrolysed with hydrochloric acid. The acidic solution after being freed from piperonal by extraction with ether was basified and again extracted with ether. The oily base (β-hydroxy-β-3:4-methylenedioxyphenylethylmethylamine, III) obtained from ether was converted into picronolate, which crystallised in bright yellow needles, m.p. 203°. (Found: N, 14·81. $C_{20}H_{21}O_8N_5$ requires N, 15·2 per cent).

The Hydroiodide of the Base (II).—An alcoholic solution of β-hydroxy-phenylethylamine (3 g. in 15 c.c.) was refluxed with methyl-ψ-thiourea hydroiodide (4 g.) on the steam-bath for 3 hours, when methyl sulphydrate was copiously evolved. The reaction mixture was freed from alcohol in *vacuo* and the syrupy residue was stirred with ether when it solidified to a cake. It crystallises from ethyl acetate in large colourless prisms, m.p. 133°. The substance gave a positive Sakaguchi's test for a guanidine derivative, yield 5 g. (Found: N, 13·4; I, 40·8. $C_9H_{14}ON_3I$ requires N, 13·6; I, 41·4 per cent).

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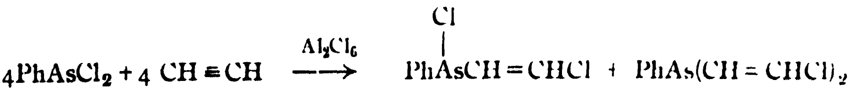
STUDIES IN ORGANO-ARSENIC COMPOUNDS. PART V. SYNTHESIS OF ARSINDOLE DERIVATIVES.

By Hirendra Nath Das-Gupta.

In a previous communication by the author (*J. Indian Chem. Soc.*, 1937, **14**, 231), the possibility of the synthesis of 1-chloroarsindole from benzene and β-chlorovinyldichloroarsine ($ClCH=CHAsCl_2$) has been shown; the intermediate compounds formed from the condensation of the reactants being two mixed arsenicals like β-chlorovinylphenylchloroarsine (I) and β-chlorovinyldiphenylarsine (III). The present paper is intended to adduce further proof in support of the mechanism of the reaction by the synthesis of the same types of intermediate compounds from a different source. The difference in this case is that one of the reactants already contains arsenic in the nucleus and that the unsaturated grouping has been introduced subsequently. When dry acetylene is passed through freshly distilled phenyldichloroarsine in the presence of anhydrous aluminium chloride, secondary and tertiary arsines are formed as usual (*cf.* Das-Gupta, *J. Indian Chem. Soc.*, 1936, **13**, 305; Green and Price, *J. Chem. Soc.*, 1921, **119**, 448; Mann and Pope, *ibid.*, 1922, **121**, 1754; Lewis and Stiegler, *J. Amer. Chem. Soc.*, 1925, **47**, 2546). In this case, however, the tertiary arsine was found to be of two different types, *viz.*, *a*) ββ'-dichlorodivinylphenylarsine (II) and (*b*) β-chlorovinyldiphenylarsine (III). Avoiding the consideration of the intermediate unstable compound of the arsine with aluminium chloride the reaction prabably takes place as follows:



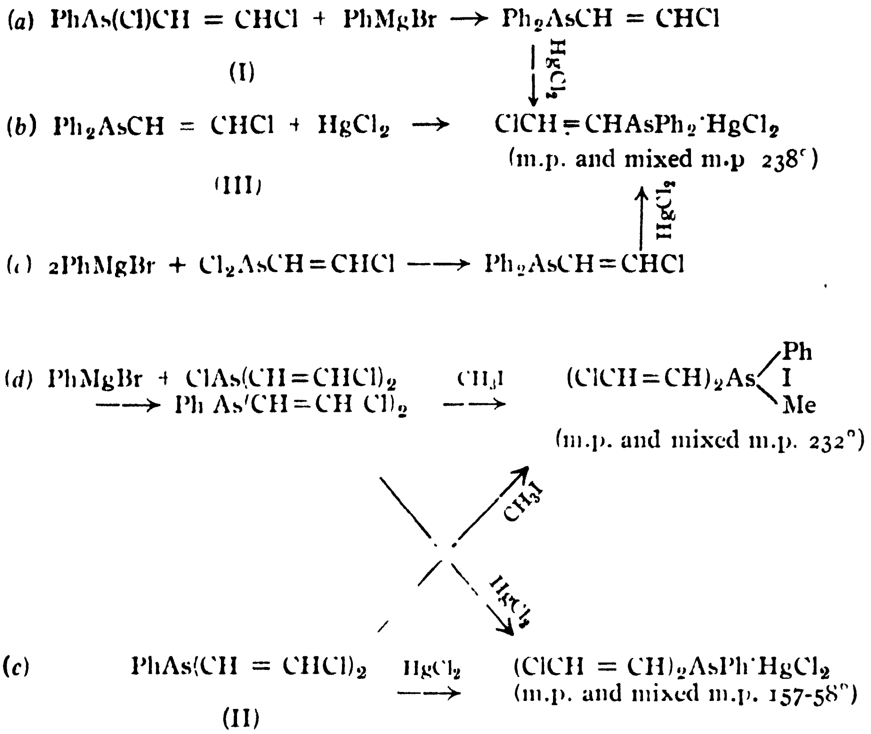
$$4PhAsCl_2 + 4\,CH\equiv CH \xrightarrow{Al_2Cl_6} Ph\overset{\overset{\displaystyle Cl}{|}}{As}CH=CHCl + PhAs(CH=CHCl)_2$$

(I) (II)

$$+\ Ph_2As\,CH=CHCl + AsCl_3$$

(III)

The following scheme shows how the identities of the different compounds have been proved.


(a) PhAs(Cl)CH = CHCl + PhMgBr → Ph₂AsCH = CHCl
(I)
HgCl₂
(b) Ph₂AsCH = CHCl + HgCl₂ → ClCH = CHAsPh₂·HgCl₂
(m.p. and mixed m.p 238°)
(III)
HgCl₂
(c) 2PhMgBr + Cl₂AsCH=CHCl → Ph₂AsCH=CHCl
(d) PhMgBr + ClAs(CH=CHCl)₂ → Ph As(CH=CH Cl)₂ CH₃I → (ClCH=CH)₂As Ph I Me
(m.p. and mixed m.p. 232°)
CH₃I
HgCl₂
(e) PhAs(CH = CHCl)₂ HgCl₂ → (ClCH = CH)₂AsPh·HgCl₂
(m.p. and mixed m.p. 157-58°)
(II)

Like other unsaturated arsenicals, the halogen attached to the β-carbon, containing a double bond, is stable. The reactivity of the chlorine, linked to arsenic, is found, though to a lesser degree, to be identical with other unsaturated derivatives, since it readily gives the arsinic acid, sulphide, cyanide, etc., but attempts to prepare the oxide by sodium ethoxide led to the formation of the ether.

1-Chloroarsindole has been synthesised from β-chlorovinylphenylchloroarsine, and 1-methyl- and 1-ethylarsindole have also been obtained from it; they are identical with the compounds derived from other sources.

EXPERIMENTAL.

β-Chlorovinylphenylchloroarsine (I) *and ββ′-Dichlorodivinylphenylarsine* (II).—Acetylene, purified by passing through a saturated solution of sodium bisulphite and concentrated sulphuric acid, was passed for 2 hours at 0° through a well-stirred mixture of freshly distilled phenylarsenious chloride (500 g.) and anhydrous aluminium chloride

(100 g.). The mixture was stirred for 7 hours more, decomposed by 20% cold hydrochloric acid and the oil separating was distilled in *vacuo* several times when the following fractions were collected : (1) 120-30°/3mm., identified to be unchanged phenylarsenious chloride. (2) 135-45°/mm. (75 g.), light yellow oil. (3) 150-55°/4mm., only 2 c.c. (4) 170-78°/5mm. (5) 195-98°/5mm. The different fractions were identified as follows : The oil, b. p. 135-45°/4mm. was identified to be *β*-chlorovinylphenylchloroarsine as it produced *β*-chlorovinyldiphenylarsine. The m. p. and mixed m. p. of the mercuric chloride double salt of the latter and that prepared synthetically were identical. [Found : C, 38·3 ; H, 2·7 ; Cl, 28·6 ; As, 30·2 ; M.W. (cryoscopic in benzene), 248·1. $C_8H_7Cl_2As$ requires C, 38·5 ; H, 2·8 ; Cl, 28·5 ; As, 30·12 per cent. M. W., 249].

The fraction boiling at 170-78°/5 mm. was identified to be *ββ'*-dichlorodivinylphenylarsine. [Found : C, 43·4 ; H, 3·09 ; Cl, 25·7 ; As, 27·6 ; M. W. (cryoscopic in benzene), 276·1, 275·9. $C_{10}H_9Cl_2As$ requires C, 43·6; H, 3·2 ; Cl, 25·8 ; As, 27·2 per cent. M. W., 275.]

Its identity was further confirmed by synthesising it from bromobenzene and *ββ'*-dichlorodivinylchloroarsine as follows : A solution of *ββ'*-dichlorodivinylchloroarsine (11 g.) in ether was added drop by drop to the Grignard reagent from bromobenzene (7 g.) and magnesium (1·2 g.) in ether (50 c c.) ; each drop reacted with slight explosive violence with the formation of a white precipitate, which dissolved on shaking. But the reaction was not so violent towards the end. The mixture was heated on a water-bath for 1 hour and then decomposed by cold water ; the ethereal layer washed successively with dilute hydrochloric acid, sodium hydroxide solution, water, dried over calcium chloride, and distilled at at 165-80°/3mm. [Found : As, 27·1; M.W. (cryoscopic in benzene), 268. $C_{10}H_9Cl_2As$ requires As, 27·2 per cent. M.W., 275].

β-Chlorovinyldiphenylarsine.—The fraction at 190-95°/5mm. was identified to be the desired compound. It gives a mercuric chloride double salt, the m.p. and mixed m.p. 238°, being identified with that prepared synthetically (*cf.* Das-Gupta, *J. Indian Chem. Soc.*, 1937, **14**, 231) (Found: As, 25·6. $C_{14}H_{12}ClAs$ requires As, 25·8 per cent).

Derivatives of β-Chlorovinylphenylchloroarsine.

β-Chlorovinylphenylarsinic acid was obtained by treating *β*-chlorovinylphenylchloroarsine with excess of hydrogen peroxide (3vol.) in glacial acetic acid and after keeping overnight the solution was evaporated to dryness on a water-bath and the residual pasty mass was dried on a porous plate and crystallised from a mixture of acetone and carbon tetrachloride, m.p. 135°. (Found: As, 30·3. $C_8H_8O_2ClAs$ requires As, 30·4 per cent).

β-Chlorovinyphenylarsine ethylether [$PhAs(OEt)\cdot CH{:}CHCl$] was prepared by heating for 20 minutes a freshly prepared alcoholic solution of sodium ethoxide (3·5 g.) and a solution of β-chlorovinylphenylchloroarsine (12 g.) in absolute alcohol (25 c.c.). The precipitate formed was filtered off and the major portion of the solvent removed by evaporation under reduced pressure. The yellow oil obtained by adding water was distilled at 165-70°/3mm. [Found: Cl, 13·2; As, 28·9; M.W. (cryoscopic in benzene), 261·3. $C_{10}H_{12}OCl$ As requires Cl, 13·7, As, 29·01 per cent. M.W., 258·5].

β-Chlorovinylphenylarsenious Cyanide was obtained by heating for 2 hours a mixture of β-chlorovinylphenylchloroarsine and excess of potassium cyanide in absolute alcohol. The solution on dilution with water gave a yellow liquid. (Found: As, 31·17. C_9H_7NClAs requires As, 31·3 per cent).

β-Chlorovinylphenylarsenious Sulphide ($ClCH = CHAs\text{-}S\text{-}AsCH = CHCl$).—A solution of β-chlorovinylphenylchloroarsine in absolute alcohol was saturated for 5 hours with dry sulphuretted hydrogen and yellow viscous oil separating was washed with alcohol. It was dissolved in acetone and treated with excess of petroleum ether and allowed to stand when needles separated, which were recrystallised from acetone, m.p. 141°. (Found: As, 32·8. $C_{16}H_{14}Cl_2As_2S$ requires As, 32·6 per cent).

β-Chlorovinyldiphenylarsine (III).—It was obtained by adding ethereal solution of β-chlorovinylphenylchloroarsine (9·6 g.) to the Grignard reagent from bromobenzene (6 g.) and magnesium (9 g.). The liquid obtained was distilled at 195-98°/4mm. The mercuric chloride double salt melts at 238°. (Found. As, 25·6. $C_{14}H_{12}ClAs$ requires As, 25·8 per cent).

β-Chlorovinylphenylmethylarsine was prepared from β-chlorovinylphenylchloroarsine and magnesium methyl iodide. It is a light yellow oil of unpleasant odour. (Found: As, 32·4. $C_9H_{10}ClAs$ requires As, 32·8 per cent).

Derivatives of ββ′-Dichlorodivinylphenylarsine.

The mercuric chloride double salt was obtained as a white precipitate by adding ββ′-dichlorodivinylphenylarsine in ether to the molecular proportion of mercuric chloride in the same solvent. The precipitate formed was washed with ether and crystallised as needles from hot alcohol, m.p. 157-58°. (Found: Hg, 36·5. $C_{10}H_9Cl_4$ As Hg requires Hg, 36·8 per cent).

The silver nitrate double salt was obtained by heating alcoholic solution of ββ'-dichlorodivinylphenylarsine and silver nitrate for 2 hours on a water-bath. The solution was poured into ether and filtered from the precipitated mass, which melts indefinitely at 205-12°. The mother liquor on further dilution with ether gave a pasty white precipitate, which was dried on a porous plate and crystallised from alcohol as clustered needles, m.p. 170°. (Found: Ag, 23·9. $C_{10}H_9O_3NCl_2AgAs$ requires Ag, 24·2 per cent).

ββ'-Dichlorodivinylphenylmethylarsonium Iodide (IV).—ββ'-Dichlorodivinylphenylarsine was heated in a sealed tube on the water-bath with excess of methyl iodide for 2 hours. The crystals separating were collected and crystallised from alcohol, m.p. 232°. (Found: As, 17·28. $C_{11}H_{12}Cl_2AsI$ requires As, 17·9 per cent).

Arsindole Derivatives.

1-Chloroarsindole.—(*a*) It was prepared (*cf.* part IV) from β-chlorovinylphenylchloroarsine in presence of anhydrous aluminium chloride in dry carbon disulphide. The fraction boiling at 135°-40/5 mm. was collected.

(*b*) β-Chlorovinylphenylchloroarsine (10 c. c.) was heated under reflux for 4 hours at 230°-40° when hydrogen chloride was evolved. The black mass was extracted several times with ether, the solvent evaporated off and the oil distilled at 132°-140/5 mm. [Found: As, 35·1; M.W. (cryoscopic in benzene), 217·4. C_8H_6ClAs requires As, 35·2 per cent. M.W., 212·5].

1-*Methylarsindole* was prepared in accordance with the method given in Part IV. The mercuric chloride double compound melts at 150-51°, identical with that from other source. (Found: As, 39·1. C_9H_9As requires As, 39·06 per cent). Picrate, m.p. and mixed m.p. 106-7°.

1-Ethylarsindole.—It was prepared from 1-chloroarsindole and ethyl magnesium iodide in a manner similar to that for 1-methylarsindole. The compound was extracted with ether, the solvent removed and the oil distilled at 138-45°/6mm. Like the methyl derivative it also possesses a very strong offensive smell and produces blister on the skin which is very difficult to heal. [Found: As, 36·3; M.W. (cryoscopic in benzene), 210. $C_{10}H_{11}As$ requires As, 36·4 per cent. M.W., 206]. It readily gives a picrate, m.p. 100-2°.

My thanks are due to Dr. M. Goswami and to Mr. B. C. Ray for their keen interest in this investigation.

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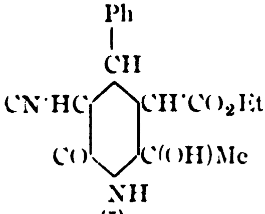
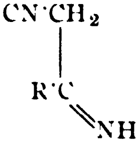
A MODIFICATION OF THE GUARESCHI PYRIDINE SYNTHESIS. PART II.

Nirmalananda Palit.

In Part I of this work (*J. Indian Chem. Soc.*, 1937, **14** 219) it was shown that under the influence of diethylamine, cyanoacetamide adds to ethyl benzylideneacetoacetate to form a ring compound (I) which presumably is the primary reaction preceding the formation of pyridines by Guareschi's method.


(I)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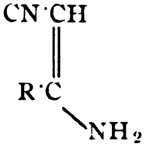
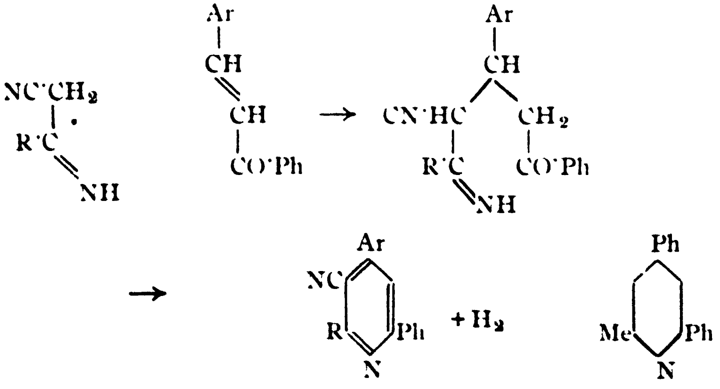
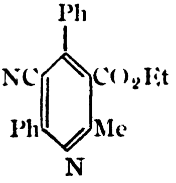

(III)

This intermediate compound was found to be uncommonly stable and the reactivity of the amido hydrogen atom, which is responsible for the ring, closure by tautomerisation, was attributed to its position between two carbonyl groups To test this view cyanoacetamide was replaced by the dinitriles of Meyer (*Chem. Zentl.*, 1908, **II**, 591) which can react in both the forms (II) and (III). The reaction would be parallel to one already studied by Meyer (*loc. cit.*) in which the dinitrile was condensed with an arylideneacetophenone in presence of sodium ethoxide.

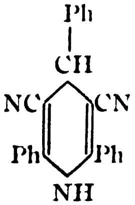

(IV) (V)

Gastaldi (*Gazzetta*, 1922, **52**, 169, 305) has thrown considerable doubt upon the constitution of these products. He prepared 2.4-diphenyl-6-methylpyridine (V) from the corresponding pyryllium salt and found it to be different from the product obtained by Meyer by hydrolysis of IV (Ar = Ph; R = Me) followed by removal of carbon dioxide. The problem was, therefore, taken up in more detail to be described in a separate communication the result of which indicates that Meyer's mode of representing the reaction is not incorrect. If that is so, benzylideneacetoacetic ester would be expected to behave in an analogous way, but sodium ethoxide failed to bring about any condensation at the room temperature and if warmed the unsaturated keto-ester was decomposed. With diethylamine, however, the condensation has been effected and a product ($C_{18}H_{24}O_6$), m.p. 152°, is obtained and this has been identified to be benzylidenebis-acetoacetic ester whichever dinitrile is used. It shows that the dinitrile does not take part in the reaction at all. A decomposing influence of organic bases on the olefine keto-ester of a different nature has been previously recorded by Ruhemann (*J. Chem. Soc.*, 1903, **83**, 374).

Several attempts to bring about the desired reaction failed with different condensing agents and at last Kohler and Souther's method (*J. Amer. Chem. Soc.*, 1922, **44**, 2903) using sodium methoxide seemed to prove more fruitful. The product in every case is a sticky semisolid complex mixture which does not solidify even on prolonged standing in ice and is difficult to purify. Thus with benzoacetodinitrile (II, R = Ph) the product is a mixture of the pyridine (VI) and the dihydropyridine (VII) obtained previously by Meyer (*loc. cit.*).



(VI)



(VII)

No trace of a compound of intermediate aldol structure could be isolated. This is in harmony with the view suggested above.

In the above condensations, benzylidene cyanoacetic ester has also been used which is stable towards sodium ethoxide and consequently gives much better yields of pure products.

EXPERIMENTAL.

Reactions with Ethyl Benzylideneacetoacetate.

(*a*) With *β-Amino-β-phenylacrylonitrile* : ***Formation of*** 3 : 5-***Dicyano-*** 2:4:6-*triphenyldihydropyridine* ***and*** 5-***Cyano-***3-***carbethoxy-***2-***methyl-***4 : 6-*diphenylpyridine*.—A methyl alcoholic solution of the dinitrile and the ester was treated with a few drops of methyl alcoholic sodium methoxide to give a distinct alkaline reaction. The reaction was not complete even on keeping for more than a fortnight. A subsequent heating on a water-bath facilitated the reaction. If heating was done earlier the decomposition products increased at the sacrifice of the pyridine. However in each case the alcohol on evaporation left a sticky semisolid A solution of it in the minimum quantity of glacial acetic acid deposited on cooling a very small quantity of a pale greenish crystalline powder, m.p. 268°. (Found: C, 83·4 ; H, 5·0 ; N, 11·8. $C_{25}H_{17}N_3$ requires C, 83·2 ; H, 4·7; N, 11·7 per cent). The mother liquor on evaporation gave the same non-crystallisable sticky mass. After boiling for a few minutes with dilute hydrochloric acid, the extract on cooling gave white needles of the cyanoketone produced by hydrolysis of the iminonitrile. It crystallised from benzene, m.p 189°. (Found: C, 76·02; H, 5·6; N, 8·43. $C_{22}H_{18}O_2N_2$ requires C, 77·19; H, 5·29 ; N, 8·19 per cent).

(*b*) *With β Amino β-p-tolylacrylonitrile*.—The sticky mass obtained by evaporating the condensation mixture was boiled with dilute hydrochloric acid. The solid obtained crystallised from acetone in large plates, m p. 189°. (Found: C, 77·78; H, 5·9 ; N, 7·8. $C_{23}H_{20}O_2N_2$ requires C, 77·52; H, 5·6 ; N, 7·86 per cent).

(*c*) *With β-Amino-p-anisylacrylonitrile* —The solid obtained by boiling with dilute hydrochloric acid was twice crystallised from alcohol, m.p. 190-92°, after shrinking at 187°. (Found: C, 73·92 ; H, 5·63 ; N, 7·8. $C_{23}H_{20}O_3N_2$ requires C, 74·19 ; H, 5·38 ; N, 7·51 per cent).

Reaction with Ethyl Benzylidenecyanacetate.

(*a*) *With β-Amino-β-phenylacrylonitrile: Formation of Diethylammonium salt of* 3:5-*Dicyano*-2-*keto*-4:6-*diphenylpiperidine* (*cf*. part I).—0·1 Mole of each were dissolved in absolute alcohol and a few drops of diethylamine added. Next day a crystalline deposit was obtained More of diethylamine was added till its smell persisted. The colourless crystals were filtered after two days (1·5 g.), and crystallised from alcohol, m p. 208-10°. Boiling acetic anhydride gave the same pyridone as below. (Found: C, 74·37; H, 6·19; N, 15·45. $C_{23}H_{22}ON_4$ requires C, 74·59; H, 5·94; N, 15·13 per cent).

Hydrolysis of the above Compound: Formation of 3:5-Dicyano-4:6-diphenyl-$\Delta^{3:6}$-dihydro 2-pyridone.—With dilute caustic soda strong ammoniacal smell was given out in the cold and when heated the evolution of the gas was copious. Nessler's reagent was unaffected by it. The reaction was quickly over. The residue crystallised from a large volume of alcohol as a voluminous mass, m p. 250-51°. (Found: C, 76·45; H, 4·10; N, 14·44. $C_{19}H_{11}ON_3$ requires C, 76·76; H, 3·70; N, 14·14 per cent).

(*b*) *With β-Amino-β-p-tolylacrylonitrile: Formation of 3:5-Dicyano-4-phenyl-6-tolyl-$\Delta^{3:6}$-dihydro-2-pyridone* (*cf.* part I).—The dinitrile (1·6g.) was added to absolute alcohol in which sodium (0·23 g.). was added. On adding the unsaturated ester (2 g.) to the suspended nitrile, the colour deepend to brownish yellow and quickly the whole went into solution. It was boiled under reflux on a water-bath for two hours, the alcohol evaporated and the residual jelly treated with water. A white precipitate was obtained, which crystallised from glacial acetic acid, yield quantitative, m.p. 293°. (Found: C, 76·91; H, 4·52; N, 13·65. $C_{20}H_{13}ON_3$ requires C, 77·17; H, 4·18; N, 13·5 per cent).

(*c*) *With β-Amino-p-anisylacrylonitrile.*—The product crystallised from a large volume of acetone or glacial acetic acid as yellow mesh of needles, m.p. 296°. (Found: C, 73·10; H, 4·31; N, 13·0. $C_{20}H_{13}O_2N_3$ requires C, 73·39; H, 4·0; N, 12·78 per cent).

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SIMULTANEOUS DETERMINATIONS OF CHLORINE, NITROGEN AND ARSENIC IN ORGANO-ARSENIC COMPOUNDS.

By Hirendra Nath Das-Gupta.

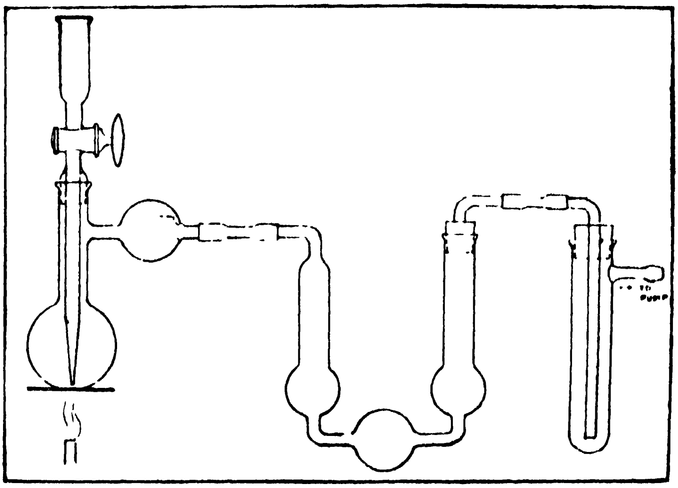
The present work was undertaken with a view to find out a suitable method for the simultaneous and rapid determinations of arsenic, nitrogen, and chlorine, the latter being attached to arsenic. Of these three elements the chlorine linked to arsenic deserves special attention. The extreme ease and rapidity with which this element undergoes changes renders its determination difficult by most of the existing methods. In order to shorten time several processes, outlined by different investigators, were tried but without any satisfactory results. Robertson's method (*J. Chem. Soc.*, 1915, **107**, 902) gave unsatisfactory results on account of very rapid evolution of hydrogen chloride which could not be trapped in the absorption tubes. Similarly Nomura and Murais' method (*Bull. Soc. chim.*, 1924, **35**, 217) presented the same difficulties as in Robertson's process. By applying ter Meulen's method (*Rec. trav. chim.*, 1928, **47**, 698) it was observed that the catalyst was coated with a deposit of metallic arsenic and that the reactions in many cases were not complete and even with the same substance varying results were obtained which were gradually on the decrease. If, however, asbestos fibres be placed on either sides of the catalyst, the results obtained are more or less comparable.

The process is based on the fact that organic compounds, containing the above mentioned elements, are decomposed when treated with a mixture of potassium sulphate, sulphuric acid and a little metallic selenium as a catalyst, with the liberation of hydrogen chloride and selenium chloride which are quantitatively absorbed in alkaline hydrogen peroxide. The absorbed chloride may be estimated either volumetrically or gravimetrically. In the latter case, however, the associated selenium should be first precipitated by sodium bisulphite. Arsenic and nitrogen are retained by the sulphuric acid mixture. The nitrogen in the digestion flask is liberated as ammonia and is estimated by the usual method. The arsenic left is first of all reduced to trivalent state by sodium bisulphite and then titrated iodimetrically after separating the precipitated metallic selenium. The digestion period is only from 25-35 minutes but the duration depends solely on the nature of the substances to be treated and in cases of volatile compounds, this should be increased so as to avoid loss by volatilisation of the original compounds.

EXPERIMENTAL.

The Apparatus.—A flask of 250 c.c. capacity was used for effecting the digestion of the compound. It was fitted with a ground-glass joint to which was attached a stoppered funnel (10 c.c.), the stem reaching nearly to the bottom and ending in capillary and the exit-tube contained a trap at the middle. The absorption apparatus consisted of a simple modification of the well-known Peligot bulb-tube and a second smaller tube which served as a guard. This was connected to a water-jet pump.

FIG. 1.



Reagents required are pure sulphuric acid, pure potassium sulphate, 15 % sodium hydroxide solution, hydrogen peroxide free from chloride, and pure metallic selenium. It is advisable to carry out a blank experiment with the reagents mentioned to ensure that the materials are free from chloride, arsenic and nitrogen under exactly the same conditions as in actual estimation.

Procedure.—The substance (0·1 – 0·2 g.) was accurately weighed out into the digestion flask and 7-8 g. of pure potassium sulphate and 5-10 mg.

of metallic selenium were introduced into the flask. The ground-glass joint, lubricated with syrupy phosphoric acid, was fixed into position and the flask was connected with the system of absorption tubes. The first absorption tube contained 15 c.c. of 15% sodium hydroxide solution, containing an equal volume of hydrogen peroxide, and the second tube contained 10 c.c. of alkali solution with the same volume of the peroxide. The funnel was filled with 10 c.c. of concentrated sulphuric acid and the pump started, when the sulphuric acid came down. The flask was allowed to remain for 15 minutes with occasional shaking and then heated slowly over a small flame. The contents of the flask at first became dark, which gradually turned colourless or light yellow after passing through intermediate shades of colour. During the whole operation a stream of air should be maintained and its rate increased towards the end. The acid mixture should boil during the last stage and the boiling should be prolonged for 5 minutes more after complete digestion. The different elements were then estimated as described below.

Estimation of Chlorine.—The contents of the absorption tubes were washed into a beaker and the chlorine estimated either gravimetrically or volumetrically. In the former case the solution was boiled to expel the hydrogen peroxide, treated with 1 c.c. of a saturated solution of sodium bisulphite solution and after 2-3 minutes gradually acidified with nitric acid The solution was then filtered from precipitated selenium and the excess of silver nitrate solution added The precipited silver chloride was filtered into a weighed Gooch crucible, washed, dried and weighed in the usual manner. In the latter case, the solution was boiled, acidified with nitric acid and 10 c.c. (or more) of *N*/10-silver nitrate solution added, filtered from the precipitated chlorides and the excess of silver titrated back with *N*/10-ammonium thiocyanate solution in the usual manner.

Estimation of Nitrogen.—The ammonia present in the digestion flask was expelled with strong solution of sodium hydroxide and was estimated as in the method of Kjeldahl.

Estimation of Arsenic.—The contents of the digestion flask after removal of ammonia were washed into a bigger vessel and 10 c.c. of a saturated solution of sodium bisulphite added and then acidified slowly by sulphuric acid. The solution was boiled to expel all the sulphur dioxide, cooled and filtered from the precipitated selenium. The filtrate was neutralised by excess of sodium bicarbonate and the arsenic was titrated by *N*/20-iodine solution. (1 c.c. of *N*/20-iodine = 0·001875 g. of arsenic).

The following table shows the nature of the results obtained in the cases of substances examined by this method :

Compound.	Chlorine		Arsenic		Nitrogen	
	Found.	Calc.	Found.	Calc.	Found.	Calc.
Methyldichloro-A	43·89 %	44·00 %	46·3 %	46·5 %		
Ethyldichloro-A	40·6	40·5	42·6	42·8		
β-Chlorovinyldichloro-A	51·08	51·31	36·2	36·1		
ββ′-Dichlorodivinylchloro-A	45·8	45·6	32·1	32·1		
ββ′β″-Trichlorotrivinyl-A	40·75	41·4	28·8	28·9		
ββ′-Dichlorodivinylmethyl-A	33·5	33·31	35·4	35·2		
Phenyldichloro-A	31·6	31·8	33·5	33·6		
m-Nitrophenylarsonic acid	—	—	30·4	30·3	5·5	5·6
o Nitrophenylarsonic acid	—	—	30·1	30·3	5·48	5·6
p-Nitrophenylarsonic acid	—		30·2	30·3	5·45	5·6

(A stands for arsine)

This method is not applicable, however, to the estimations of bromine and iodine in the corresponding organo-arsenic halides.

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CONSTITUTION OF THE SEEDS OF *BLEPHARIS EDULIS*, PERS. PART II. THE COMPOSITION OF THE OIL

By G. P. Pendse and Jagraj Behari Lal.

A bitter glucoside *Blepharin* ($C_{16}H_{20}O_{11}$, m.p. 222°) and *dl*-allantoin were isolated from the seeds of *Blepharis edulis*, Pers (Lal, *J. Indian Chem. Soc.*, 1936, **13**, 109). The present paper deals with the composition of the oil obtained from the seeds by exhaustive extraction with benzene. It has been found that the oil contains oleic and linolic acids in the unsaturated portion and palmitic, stearic and arachidic acid in the saturated portion of the fatty acids. The unsaponifiable matter is identified to be a sterol. The oil on standing for over three days deposited a sterol identified to be arnidiol (*cf.* Klobb, *Compt. rend.*, 1904, **138**, 763; 1905 **140**, 1700).

EXPERIMENTAL.

9 Kg. of the powdered seeds on exhaustive extraction with benzene yielded 342 g. (3·8%) of a thick reddish brown oil possessing the characteristic odour of the drug. The crude oil was purified in the usual way. It deposited a small amount of a light brown solid on standing for 2-3 days. It is free from nitrogen or sulphur and has been found to belong to the class of semi-drying oils. The chemical and physical constants of the oil are given in Table I. 150 G. of the oil were saponified in the usual way. The constants of the fatty acids are given in Table II.

Table I.

Optical rotation	$[\alpha]_{D,}^{28}$ − 8·4	Sapon. value	186·5
Sp. gr.	0·9332 at 28°	Acetyl value	11·54
Viscosity	8·35 (compared to Rape oil)	Hehner's value	91·65
Ref. index	1·4846 at 30°	Iodine value	90·8
Solidifying point	−3°	Unsaponifiable matter	2·5−3%
Acid value	11·85		

TABLE II.

Consistency	Semi-solid.	Neutralisation value	180·8
Sp. gr.	0·9054 at 30°	Mean M. W.	309·5
Ref. index	1·4796	Iodine value	92·5

The mixture of the fatty acids was then separated into the saturated and unsaturated acids by Twitchell's method (*Ind. Eng. Chem.*, 1921, **13**, 806). During the separation of the acids a small amount of a resinous mass, insoluble in ether, was separated. Table III gives the percentage, mean M. W. and iodine values of the saturated and unsaturated acids.

TABLE III.

Acids.	% of the mixed acids.	% in the oil.	Iodine value.	Mean M. W.
Saturated	12·38	11·34	2·6	276
Unsaturated	87·62	80·3	104·7	270·2

Examination of the Unsaturated Acids.

The unsaturated acids were systematically examined by oxidation with potassium permanganate. The absence of hexahydroxystearic acid proved the absence of linolenic acid. Two acids, dihydroxystearic acid and tetrahydroxystearic acid, were isolated by extraction with ether and hot water. These two acids showed the presence of oleic and linolic acids in the mixed liquid acids.

The quantitative examination of the unsaturated acids was done by the method of Jamieson and Baughman (*J. Amer. Chem. Soc.*, 1920, **42**, 1197) by preparing their bromo-addition products. The hexabromo derivative of linolenic acid is insoluble in cold ether; since no precipitate insoluble in ether was found, the absence of linolenic acid was confirmed. The ether-soluble portion was dissolved in petroleum ether and cooled when crystals of linolic tetrabromide (m. p. 113-14°) separated showing the presence of linolic acid. The residue was evaporated to dryness and the bromine content estimated. Table IV gives the results of the analysis of the bromo-addition products.

TABLE IV.

Wt of the unsaturated acids	4·4632 g.
Linolic acid tetrabromide	1·2364
Residue (di- and tetrabromides)	6·0138 (Br, 36·68%)
Dibromo-oleic acid in the residue	5·8388 (97·1%)
Tetrabromolinolic acid in the residue	0·1749 (2·9%)
Total tetrabromolinolic acid	1·4113
Linolic acid equivalent to the tetrabromide	0·7305 (16·37%)
Oleic acid equivalent to the dibromide	3·7252 (83·45%)

The iodine value of the mixture of the unsaturated acids was found to be 104·7. Table V contains the percentage of the linolic and oleic acids calculated by the bromine addition method and from the iodine values.

TABLE V.

	Bromine addition method.			Calc from the iodine values.		
	In the unsaturated acids.	In the total fatty acids.	In the original oil	In the unsaturated acids.	In the total fatty acids.	In the original oil
Oleic acid	83·45%	72·75%	66·66%	83·93%	73·16%	67·04%
Linolic acid	16·37	14·27	13·08	16·07	14·00	12·83

Examination of the Saturated Acids.

The saturated acids separated from the mixed acids were freed from traces of liquid acids by pressing over a porous plate. The acids, thus obtained, are yellowish white in colour, m. p. 54-55°.

The mixture of the acids was converted into the methyl esters and 10 g. of the esters were distilled under reduced pressure. The iodine values and the saponification values of the different fractions were determined and the mean M. W. calculated. The mean molecular weight of methyl palmitate is 270·3 and that of methyl stearate 298·4. The mean molecular weights of the first three fractions lie between these two values and therefore indicate a mixture of the two. The mean molecular weight of the last fraction is greater than

298 and hence contains the ester of an acid of higher molecular weight. The free acid obtained from the last fraction melted at about 71-73 , pointing it to be a mixture of arachidic acid and stearic acid. The percentages of the acids were determined in the different fractions by means of their iodine values and mean molecular weights (*J. Amer. Chem. Soc.*, 1920 **42**, 152). Tables VI and VII contain the results of the analysis.

TABLE VI.

Fractions.	B. p.	Wt. of fractions.	M. p. of free acids.
1	180-200°/1·5 mm.	2·28 g.	63-64°
2	200-20°/1 mm.	3·64	64°
3	220-35°/1 mm.	0·84	66 68°
4	Residue above 240°	3·24	71-73°

Examination of the Unsaponifiable Matter.

The unsaponifiable matter (3%) was dissolved in ether and washed with water repeatedly to remove the adhering soap. The dried ethereal solution was distilled when a yellowish white sticky matter was obtained. On repeated crystallisations from alcohol white silky flakes were obtained, m. p. 115-117°, $(\alpha)_D^{30}$ (in chloroform), −35°. From the colour reactions the unsaponifiable matter was identified to be a phytosterol. [Found : C, 78·0 ; H, 10·33. $C_{27}H_{47}O, 2H_2O$ (?) requires C, 77·92 ; H, 10·6 per cent].

TABLE VII.

Fraction.	Iodine values.	Sapon. value.	Mean M. W.	Esters of unsaturated acids.	M. W. of saturated acids.	Palmitic acid.	Stearic acid.	Arachidic acid	Unsaturated acid.
1	2·4	203·68	275·5	2·423% (0·055 g.)	275·25	1·735 g. (76·18%)	0·38 g (16·39%)	......	0·052 g. (2·3 %)
2	1·6	198·46	282·8	1·615% (0·059 g.)	282·8	2·20 (60·31%)	1·21 (33·14%)	......	0·057 (1·53%)
3	1·2	192·6	291·35	1·22% (0·01 g.)	291·4	0·20 (23·2%)	0·59 (74·18%)	......	0·0095 (1·16%)
4	0·8	187·2	299·7	0·81% (0·03 g.)	299·8	......	3·03 (93·62%)	0·029 (0·9%)	0·0285 (0·8%)

Examination of the Solid separated from the Oil.

The light brown solid which was deposited from the oil was filtered and pressed on a porous plate. It was then washed with benzene in the cold to remove the adhering oil. A light brown coloured amorphous solid (1 g.) was thus obtained. The amorphous powder was extracted repeatedly with boiling alcohol which on cooling deposited a crystalline solid, m. p. 249-50°. A little of the amorphous powder was insoluble in alcohol and did not yield any crystalline product.

The crystalline solid answered to Salkowskis's test, hydrochloric acid test, and Burchard-Liebermann's tests and was proved to be a phytosterol. The sterol appears to be identical with arnidiol described by Klobb (*loc. cit.*). [Found : C, 79·86; H, 11·26. $C_{28}H_{44}(OH)_2$ requires C, 81·15; H, 11·11 per cent].

Sterol from *Blepharis edulis* oil.	Arnidiol.
M. p., 249-50°	M. p, 249-50°
$[\alpha]_D^{15}$, –61·5 (in chloroform solution)	$[\alpha]_D^{32}$, –62·8
Diacetyl derivative, m p. 96-98°	Diacetyl derivative, m. p. 100°

The authors take the opportunity of expressing their indebtedness to Dr. S. Dutt of the Allahabad University for his valuable help and guidance throughout the investigation. One of us (G. P. P.) is thankful to the authorities of the Victoria College for the facilities given to him.

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/CHEMICAL EXAMINATION OF THE FRUITS OF *SOLANUM NIGRUM*, LINN PART I. THE COMPOSITION OF THE OIL FROM THE SEEDS.

By G. P. Pendse.

Solanum nigrum (N. O. *Solanaceae*), known in Hindustani as *Gurkamai* and *Chhoti Makoi*, is widely cultivated in India. The description of the plant and its medicinal properties are given in detail by Dymock (*"Pharmacographica Indica,"* 1891, **II**, 549) and Basu and Kirtikar ("Indian Medicinal Plants," 1918, **II**, 889). The berries of the plant are of great importance in Hindu medicine as being useful as a tonic, and in heart diseases, in fevers, diarrhoea, eye diseases, chronic enlargement of the liver and various other ailments.

Genevil and Desforses (*cf.* Dymock, *loc. cit.*) isolated the active principle of these fruits and assigned to it the formula $C_{45}H_7O_{16}N$ and named it as solanine, The present paper deals with an account of the fixed oil obtained from the seeds of the fruits. The juice, the husk and the oil-free seeds are under investigation.

EXPERIMENTAL.

20 Kg. of the fresh fruits yielded: juice, 6 litres (30%); husk (dried), 0·75 kg. (3·75%); seeds, 1·9 kg. (9·5%).

The powdered seeds (1·9 kg.) on exhaustive extraction with petroleum ether (b.p. 56-60°) yielded about 380 g. (about 2%) of a greenish-yellow oil having characteristic odour of the drug. The crude oil was purified in the usual way with animal charcoal and Fullers' earth. The oil is free from nitrogen and sulphur and has been found to belong to the Drying class of oils. The physical and chemical constants are given in Table I.

TABLE I.

α^{28}_{D} (in alcoholic solution),	−6·61	Sapon. value	184·7
Sp. gravity	0·8964 at 30°	Acetyl value	9·97
Viscosity	7·12 (compared to rape oil)	Hehner's value	93·10
Ref. index	1·4436 at 30°	Iodine value	111·7
Solidifying pt.	−7°	Unsaponifiable	
Acid value	2·4	matter	1·4−1·6%

150 G. of the oil were saponified with alcoholic potash and the unsaponifiable matter extracted with ether. The fatty acids were liberated and purified in the usual way. Table II gives the constants of the mixed fatty acids.

TABLE II.

Consistency.	Liquid.	Neutralisation value	183·4
Sp. gravity	0·8682 at 30°	Mean M. W.	305·2
Ref. index	1·4125 at 30°	Iodine value	112·4

The mixture of the fatty acids was then separated into the saturated and unsaturated acids by Twitchell's method (*Ind. Eng. Chem.*, 1921. **13,** 806). During the separation a small quantity of resinous mass insoluble in ether was separated. Table III gives the percentage, mean M. W. and iodine values of the saturated and unsaturated acids.

TABLE III.

Acids.	% in the mixed acids.	% in the oil.	Iodine value	Mean M.W.
Saturated	5·88	5·48	3·6;	280·4
Unsaturated	94·12	87·62	114·8	276·6

Examination of the Unsatuıated Acids.

The unsaturated acids were systematically analysed qualitatively by oxidation with potassium permanganate. Hexahydroxystearic acid could not be detected in the oxidation products showing thereby the absence of linolenic acid. Ether extracted a crystalline acid (m.p. 134-36°) which was identified as dihydroxystearic acid. The ether insoluble portion on extraction with boiling water yielded an acid (m.p. 170-72°), which was proved to be tetrahydroxystearic acid. The formation of these two acids and the absence of hexahydroxystearic acid prove the presence of linolic and oleic acids and the absence of linolenic acid in the unsaturated acids.

The quantitative estimation of the acids was done by the bromine addition products by the method of Jamieson and Baughmann (*J. Amer. Chem. Soc.*, 1920, **42,** 1197). Table IV gives the results of the analysis of the bromine addition products.

TABLE IV.

Wt. of the unsaturated acids taken	... 4·7378 g.
Linolenic hexabromide insoluble in ether	... Nil.
Linolic tetrabromide (m p. 113-14°)	.. 1·8636 g.
Residue (dibromide and tetrabromide)	.. 6·0352 (Br, 38·02%)
Dibromo-oleic acid in the residue	... 5·340 (89·37%)
Tetrabromolinolic acid in the residue	... 0·6412 (10 63%)
Total tetrabromolinolic acid	... 2·5048
Linolic acid equivalent to tetrabromide	... 1·2958 (27·36 %)
Oleic acid equivalent to dibromide	... 3·4406 (72·63 %)

The proportions of the linolic and oleic acids in the unsaturated acids were also determined from the iodine value of the liquid acids. Table V contains the percentage of the two acids calculated by the bromine addition method and also from the iodine value of the mixture.

TABLE V.

	Bromine addition method.			Calculated by iodine value.		
Acids	In the mixed unsaturated acids.	In the total fatty acids	In the original oil	In the mixed unsaturated acids.	In the total fatty acids.	In the original oil.
Oleic	72·63%	68·36%	63·63%	72·85%	68·54%	63·83%
Linolic	27·36	25·75	23·97	27·15	25·56	23·79

Examination of the Saturated Acids.

The mixture of the saturated acids was freed from traces of liquid acids by pressing it over a porous plate. The saturated acids were converted into their methyl esters and about 8 g. of the esters were fractionally distilled under reduced pressure. The saponification values of the different fractions were determined and the mean molecular weight calculated. The acids were liberated from the different fractions and their melting points determined. The presence of palmitic and stearic acids only could be shown in the mixture of saturated acids. Table VI contains the results of these experiments.

TABLE VI.

Fraction.	B p.	Wt. of the fraction.	Sapon value.	Mean M. W.	Acids		M.p, of liberated acids.
					Palmitic	Stearic	
1	170°-185°/1 mm.	2·64 g.	202·4	277·2	1·90 g. (71·56%)	0·62 g. (23·4%)	63-65°
2	185-200°/0·7 mm.	1·52	196·6	285·4	0·68 g. (43·87%.	0·80 g. (51·21%)	64-66°
3	Residue	3·84	190·8	294·1	0·52 g. (14·5%)	3·12 g. (80·71%)	67-68°

Examination of the Unsaponifiable Matter.

The unsaponifiable matter (1·5%), obtained from the soap solution by means of ether. was washed in ethereal solution with water. The dried ethereal solution was next distilled when white silky flakes were obtained. It was crystallised from alcohol as colourless silky flakes, m.p. 127—29′. The *acetyl* derivative was prepared in the usual manner, m.p. 119—20°. The optical rotation in alcoholic solution was $(\alpha)_D^{32} = -30{\cdot}5°$. The unsaponifiable matter gave the colour reactions of a phytosterol.

The author takes this opportunity of expressing his indebtedness to Dr. S. Dutt of the Allahabad University for his valuable guidance, to Dr. N. Ghatak for his kind interest in the investigation, and to the authorities of the Victoria College, Gwalior, for the facilities given to him.

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WEIGHTING OF INDIAN SILK.

By C. R. N. Reddy and B. S. Srikantan.

Weber (*Textilber.*, 1936, **17**, 147) has made a detailed study of the tin weighting process on silk fibres and considers that stannic phosphate formed as a result of the action of the unhydrolysed stannic chloride and the di-sodium phosphate of the fixing bath has got a detrimental effect on the fibres. Attempts have been made to substitute tin with other heavy metals like zinc (Berg and Imhoff, U.S.P., 1926, 1579628) and lead (Berg, Imhoff and Heiberg, U S.P., 1935, 1990449, and 1990450). But in these patents a treatment with tin as a preliminary to the process is considered necessary. However, a more recent patent (Rotheli, U.S.P., 1935, 2010324), in weighting with lead under certain experimental conditions covered by the the patent, completely avoids the use of tin. It is claimed that a weighting of 200% is obtained without adversely affecting the tensile strength of the fibres.

In India silks are not generally weighted before selling but the bulk of them are sold in a raw state (private communication from the sericultural expert, Madras). The following paper describes the results of a detailed study of the conditions of the weighting of Indian silk with lead acetate directly. Two varieties of silk locally known as *Eri*-silk and the Mysore-Japanese cross were chosen for the study.

EXPERIMENTAL.

Weighting Procedure.—Exactly weighted quantities of silk (usually 0·5 g.) were kept immersed in 50 c.c. of the weighting solution for a definite time. Then the fibres were thoroughly washed with large amounts of water and were dried at 78° in an air oven for one hour. The increase in weight noted and the percentage weighting calculated. The fibres before weighting were also kept in the drying chamber and it was assumed that the humidity of atmosphere did not vary appreciably during the days the experiments were conducted. The density of the weighting solution was noted by means of Westphal balance.

Breaking Strength.—Instead of measuring the tensile strength as such, the weight necessary to break a definite length of the fibre under free suspension was noted. Six inches of fibre were suspended by corks held in a clamp. Weights were added to a small pan at the other end till the fibre snapped. The weight of the pan together with that of the added weight was taken as the breaking strength of the fibre. For each sample a number of readings were taken and the average value of the breaking strength was recorded. For the untreated *Eri*-silk it was 95 g. and for untreated *Mysore-Japanese cross* it was 100 g. The individual readings did not vary more than 2%.

The Optimum Hydrogen-ion Concentration of the Weighting Bath.— Different strengths of lead acetate solutions were brought to various p_H values by the addition of 25% ammonium hydroxide. The p_H was determined colorimetrically with cresol-red as the indicator. The following table gives the relation between the p_H values of the weighting solution, the increase in weight and the tensile strength of the treated fibres.

TABLE I.

Mysore-Japanese cross silk.

Time of weighting = 1 hr. Temp. = 28·5°

	A Strength of soln. 1·75.						B. Strength of soln - 1·31.					
p_H ..	7·4	7·6	8·0	8·4	8·8	9·5	7·4	7·6	8·0	8·4	8·8	9·5
% Increase in wt	0·4	4·82	7·0	8·62	9·3	10·0	1·51	3·9	7·2	8·0	8·2	9·5
Breaking strength (g.) ..	100	98	100	100	96	95	96	102	114	110	100	98
Appearance ...	[. . . Fair . .]					Dull.	[... ... Fair ... ...]					Dull.

It is seen from the above table that considering the quality of the silk after weighting in relation to its breaking strength and appearance, a p_H value between 8·4 yields the best results. In the following experiments a p_H value of 8·0 has been used throughout.

Time of Weighting.—Table II shows that weighting mostly occurs in the first half an hour and further appreciable increase is not indicated by prolonged treatment. On the contrary a further treatment has a detrimental action on the quality of the silk. In the case of the *Eri*-silk the appearance is rendered dull.

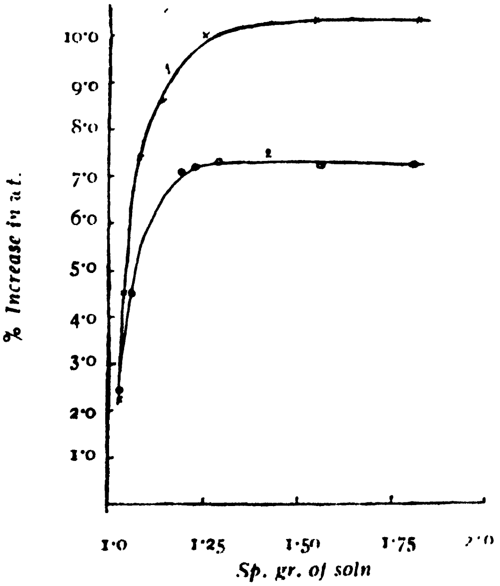
TABLE II

Temp. 28·5. p_H = 8·0.

	Silk : *Mys.-Jap. cross.*				Silk : *Mys.-Jap cross*				Silk : *Eri*		
	A. Strength of soln. = 1·56.				B. Strength of soln. = 1·05				C. Strength of soln. = 1·05.		
Time (min.) ...	15	30	60	120	15	30	60	120	30	60	120
% Increase in wt. (g.)	3·9	7·1	7·3	8·2		4·5	4·5	5·8	4·5	6·1	6·5
Breaking strength (g.)	97	125	100	96	95	100	100	96	94	92	96
Appearance ...	[... Fair...]			Dull.	[. .Fair .]			Dull.	Dull	Dull	Dark

Influence of the Concentration of the Weighting Bath.—Experiments were next performed to find the optimum concentration that would be necessary for the maximum absorption of the salt. Solutions of different strengths (p_H 8·0) were kept in crystallising basins and weighed quantities of silk were immersed in each of them for 30 minutes at a temperature of 28·5°. The data are presented in Fig. 1 for *Eri*-silk and Mys.-Jap. cross. In general it is noted that the *Eri*-silk has a higher weighting capacity than the Mys.-Jap. cross. But it acquires a deep yellow colour as soon as it is brought into contact with the lead acetate solution. The silk loses its gloss. The deep yellow colour is persistent even after the repeated washings but becomes lighter on a further treatment with sodium hydrogen phosphate or silicate. The weighting, in both cases, at first increases with the strength of the bath and soon reaches a saturation value at sp. gr. 1·25, after which it is steady.

FIG. 1.



Curves 1 and 2 refer respectively to *Eri* silk and *Mys.-Jap* silk

Influence of Temperature.—Tables III and IV shows the influence of temperature of the bath on weighting. It is evident that a variation of temperature from 20° and 40° does not appreciably affect the weighting, but it produces a considerable deterioration in the quality of the silk as seen from its appearance and its tensile strength.

TABLE III.

Eri-silk.

Temp.	Conc (sp. gr.)	% Increase in wt	Breaking strength	Remark
20°	1·05	1·24 g	98 g	Dull
	1·53	10·22	90	,,
	1·91	10·14	92	Very dull
28·5°	1·05	4·5	94	Pale yellow
	1·53	10·6	95	Dull.
	1·91	10·4	96	Very dull.
40°	1·05	3·95	95	Deep yellow
	1·50	10·34	98	,, ,,
	1·91	10·40	94	Dull yellow.

TABLE IV.

Jap.-Mys. cross silk.

Temp.	Conc (sp. gr.)	% Increase in wt	Breaking strength	Remark
20°	1·05	1·4	98	Dull.
	1·56	7·4	92	,,
	1·93	8·1	100	Very dull
28·5	1·05	1·5	95	Fair
	1·56	7·1	125	,,
	1·93	7·4	102	Not fair
40°	1·05	2·1	112	Fair
	1·56	7·2	100	,,
	1·93	8·6	102	Dull.
50°	1·56	7·6	98	Very dull

For this silk, a temperature of about 28·5° and a concentration of 1·56 (sp. gr.) seem to be the best conditions.

Maximum Weighting Capacity.—It is claimed by the patents referred to in this paper that a weighting as high as 200% could be obtained without any adverse effect on the strength of the fibres. Table V gives the maximum weighting capacity of Mysore-Japanese cross silk under the conditions described. The silk was first treated with lead acetate solution, washed well with water and then kept for 5 minutes in a fixing bath of 5° Be., of sodium hydrogen phosphate, washed well and dried. This process was repeated till it had an adverse effect on the fibres. A weighting of 105% is obtained.

TABLE V:

Sp. gr. of weighting bath = 1·32. Temp. = 28°. p_H = 8·0.

No. of treatment	..	1	2	3	4	5	6	7
% Increase in weight	...	7·4	10·0	21·2	45·06	68·24	90·43	104·86
Breaking strength (g)	...	120	110	105	105	105	105	105

SUMMARY.

1. An attempt has been made to weight two varieties of Indian silk (*Eri* and Jap.-Mys. cross) directly with lead acetate

2. The optimum hydrogen-ion concentration of the weighting bath has been found to be 8·0.

3. The weighting is mostly a quick process taking place in first few minutes but the fibres can be loaded however to an extent of 105% increase in weight by alternate weighting and fixing treatment.

4. The weighting increases till the solution has sp. gr. 1·25 after which a further increase in the strength of the solution does not affect it.

5. Variation in temperature from 20°-40° does not increase the weighting but has a bad effect on the fibres as seen from appearance and tensile strength. An optimum temperature of 28·5° is recommended.

6 In general Mysore-Japanese cross is more suitable for weighting treatment than the *Eri*-silk, since the latter acquires an undesirable deep colour and loses its tensile strength, though it is capable of getting itself weighted more than the former in the treatment.

Our thanks are due to the Sericultural expert of the Madras Industries Department for giving us the samples of silk.

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POTENTIOMETRIC STUDIES IN OXIDATION—REDUCTION REACTIONS. PART II. OXIDATION WITH POTASSIUM IODATE.

By Balwant Singh and Ijaz Ilahi.

Fenwick (*Dissertation, Ann Arbor*, 1922, p. 76) studied the oxidation of thiocyanate with iodate in the presence of concentrated hydrochloric acid using the polarised bimetallic system. In Part I of this series (Singh and Ilahi, *J. Indian Chem. Soc.*, 1936, **13**, 717) the authors have shown that thallous chloride, stannous chloride, mercurous chloride, potassium, antimonyl formate and arsenious oxide can be determined potentiometrically by titrating against standard potassium iodate in presence of concentrated hydrochloric acid. In the present investigation the work has been extended to estimate potassium thiocyanate, sodium tetrathionate, hydrazine sulphate, potassium permanganate and potassium dichromate following the same experimental technique.

EXPERIMENTAL.

A known weight of each salt was weighed into a titration vessel and the required amount of concentrated hydrochloric acid added to keep its concentration above 4 *N*. Standard potassium iodate was added from a burette, the mixture stirred by a mechanical stirrer and the progress of the oxidation followed with the potentiometer.

For the estimations of potassium dichromate and potassium permanganate, a known weight of each salt was mixed with a known excess of potassium iodide solution and the required amount of hydrochloric acid. The excess of potassium iodide was determined by titrating the mixture potentiometrically against standard potassium iodate

A series of potentiometric titrations were performed with different amounts of each salt. One titration for every salt, as typical of that set is recorded in the following tables.

TABLE I.

Titration of K-thiocyanate (0·0323 g.) mixed with 20 c.c. of water and 25 c. c. of conc. HCl against KIO_3 (*M*/10).

KIO_3.	E. M. F (volts).	*E/C* (m.volt/c.c.).
4·00 c.c.	0·552	
		50
4·20	0·562	
		65
4·40	0·575	
		85
4·60	0·592	
		90
4·80	0·610	
		110
4·90	0·621	
		160
4·95	0·629	
		5140
5·00	0·886	
		120
5·05	0·892	
		110
5·15	0·903	
		85
5·35	0·920	
		40
5·85	0·940	
		13
6·85	0·953	
		6
8·85	0·965	
		- -

TABLE II.

Titration of Na-tetrathionate (0·0270 g.) mixed with 20 c. c. of water and 25 c. c. of conc. HCl. against KIO_3 (*M*/20).

KIO_3.	E. M. F. (volts)	*E/C* (m. volt/c.c.).
5·00 c.c	0·586	
		16
6·00	0·602	
		20
6·20	0·606	
		35
6·40	0·613	
		40
6·60	0·621	
		50
6·80	0·631	
		80
6·90	0·639	
		120
6·95	0·645	
		4120
7·00	0·851	
		200
7·05	0·861	
		160
7·10	0·869	
		90
7·20	0·878	
		55
7·40	0·889	
		30
7·00	0·904	
		9
8·00	0·913	

TABLE III.

Titration of hydrazine sulphate (0·1301 g.) mixed with 20 c.c. of water and 25 c. c. of conc. HCl against KIO_3 (*M*/10).

KIO_3.	E. M. F. (volts).	*E/C* (m. volt/c.c.).	KIO_3.	E. M. F. (volts).	*E/C* (m. volt/c.c.).
8·00 c.c.	0·595		9·95 c.c.	0·694	
		18			3620
9·00	0·613		20·00	0·875	
		20			140
9·20	0·617		10·05	0·882	
		40			110
9·40	0·625		10·15	0·893	
		50			60
9·60	0·635		10·35	0·905	
		60			29
9·80	0·647		10·80	0·918	
		280			14
9·90	0·675		11·80	0·932	
		380			

TABLE IV.

Titration of $KMnO_4$ (0·0632 g.) mixed with 10 c.c. of water, 40 c.c. of KI ($M/20$) and 60 c.c. of conc. HCl against KIO_3 ($M/20$).

KIO_3	E.M.F. (volts)	E/C (m volt/c.c.)
8·00 c.c.	0·557	
		16
9·00	0·573	
		34
9·50	0·590	
		57
9·80	0·607	
		70
9·90	0·614	
		80
9·95	0·618	
		140
10·00	0·625	
		4060
10·05	0·828	
		240
10·10	0·840	
		100
10·20	0·850	
		55
10·40	0·861	
		50
10·90	0·894	
		11
11·90	0·908	

TABLE V.

Titration of $K_2Cr_2O_7$ (0·0915 g.) mixed with 10 c.c. of water, 40 c.c. of KI ($M/20$) and 50 c.c. of conc. HCl against KIO_3 ($M/20$).

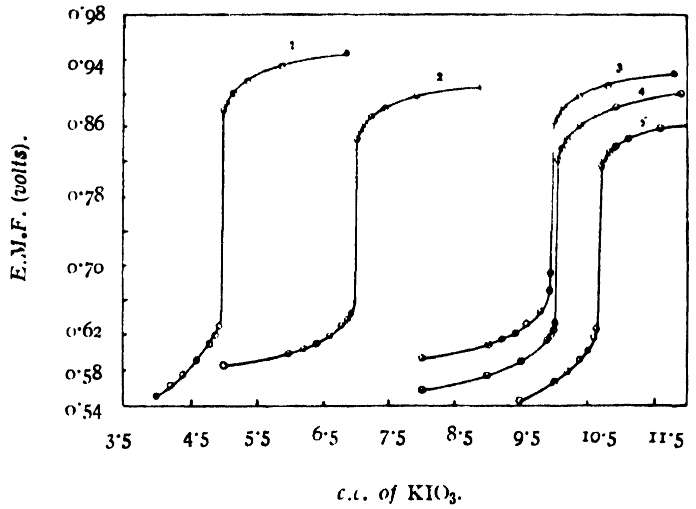
KIO_3	E.M.F. (volts)	E/C (m volt/c.c.).
9·50 c.c.	0·544	
		42
10·00	0·565	
		60
10·20	0·577	
		75
10·40	0·592	
		100
10·50	0·602	
		150
10·60	0·617	
		220
10·65	0·628	
		3860
10·70	0·821	
		180
10·75	0·830	
		140
10·80	0·837	
		70
10·90	0·844	
		60
11·10	0·856	
		22
11·60	0·867	

The curves for the above titrations are given in Fig. 1.

DISCUSSION.

In these titrations, with the addition of standard potassium iodate, the E.M.F. rose steadily till the equivalence-point. At the equivalence-point, there was a sharp jump in potential in each case. For the addition of 0·05 c.c. of the titrant, the inflection potential was of the order of 257, 206, 181, 203 and 193 millivolts for potassium thiocyanate, sodium tetrathionate, hydrazine sulphate, potassium permanganate, and potassium dichromate respectively. After the equivalence-point, there was again a rise in the potential which became steady on further addition of the reagent.

FIG. 1.



Curves 1—5 refer respectively to K-thiocyanate, Na-tetrathionate, hydrazine sulphate, $KMnO_4$ and $K_2Cr_2O_7$.

From the volume of the potassium iodate solution required in each titration, corresponding to the equivalence-point, the amount of the each salt was calculated. The values obtained are compared with the amounts of th salt taken in Table VI.

TABLE VI.

Potassium thiocyanate.		Sodium tetrathionate.		Hydrazine sulphate.	
Taken.	Found.	Taken.	Found.	Taken.	Found.
0·0323 g.	0·0322 g.	0·0270 g.	0·0269 g.	0·1301 g.	0·1299 g.
0·0685	0·0684	0·0540	0·0541	0·2168	0·2167
0·0921	0·0922	0·0712	0·0712	0·3892	0·3890
0·1182	0·1181	0·1081	0·1082	0·4731	0·4732

TABLE VI (*contd.*).

Potassium permanganate.

$KMnO_4$ (taken).	KI (*M*/20) (added).	KIO_3 (*M*/20) (used).	KI (*M*/20) (used for permanganate).	$KMnO_4$ (found).
0·0632 g.	40 c.c.	10·03 c.c.	19·94 c.c.	0·0630 g
0·0807	50	12·25	25·50	0·0806
0·0946	60	15·03	29·94	0·0946
0·1132	65	14·58	35·84	0·1133

Potassium dichromate.

$K_2Cr_2O_7$ (taken).	KI (*M*/20) (added).	KIO_3 (*M*/20) (used)	KI (*M*/20) (used for dichromate).	$K_2Cr_2O_7$ (found).
0·0915 g.	40 c.c.	10·68 c.c.	18·64 c.c.	0·0914 g.
0·1225	50	12·52	24·96	0·1224
0·0490	30	9·98	10·04	0·0492
0·0733	30	7·53	14·94	0·0732

The above results show that potassium thiocyanate. sodium tetrathionate, hydrazine sulphate, potassium permanganate and potassium dichromate can be accurately determined by the potentiometric method.

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OXIDATIVE DEAMINATION OF THE AMINO-ACIDS.

By B. C. Kar.

The oxidation of the amino-acids by potato-tyrosinase was first observed by Chodat and Schweizer (*Arch. Sci. Phys. Nat.*, 1913, **35**, 140). The products of reaction were ammonia, carbon dioxide and an aldehyde containing one carbon atom less than the original amino-acid. The rate of the above reaction was found to be much increased in the presence of certain phenols such as *p*-cresol and catechol. They explained this deamination by the direct action of tyrosinase on amino-acids and the phenols caused acceleration by combining with the reaction products (Schweizer, *Biochem. Z.*, 1917, **78**, 37). When phenols were not present, the uncertainty in the detection of ammonia and aldehyde was explained to be due to their further reaction among themselves.

On repetition of the above experiments of Chodat and Schweizer, Happold and Raper (*Biochem. J.*, 1925, **19**, 92) showed that the deamination of the amino-acids is not due to the direct action of tyrosinase but due to the formation of *o*-quinones from phenol. They investigated the effect of the addition of *p*-cresol, phenol, catechol, resorcinol, quinol and *p*-benzoquinone on the system tyrosinase—amino-acid. From the experimental results they found that only those phenols which are likely to give *o*-quinone or a derivative of it, caused deamination. They studied the action of *o*-quinone prepared by the method of Willstätter and Muller (*Ber* , 1908, **41**, 2580) under identical conditions in which the experiments were carried out in the absence of tyrosinase and found that this substance attacked the amino-acids with the production of ammonia.

Pugh and Raper (*Biochem. J.*, 1927, **21**, 1370) similarly showed that the deamination of glycine could be effected by adding *o*-homoquinone in place of *o*-benzoquinone. They showed the formation of *o*-quinones by the action of tyrosinase on catechol and certain other phenols by actual isolation.

Robinson and McCance ((*Biochem. J.*, 1925, **19**, 251) working simultaneously over the same point came to the same conclusion as Happold and Raper (*loc. cit.*). But as regards the mechanism of the reaction they did not accept the view that *o*-quinone brought about the secondary oxidation of the amino-acids ; for they observed that both the diminution of the amino-nitrogen and the production of ammonia occured in the case of glycine and resorcinol in presence of tyrosinase from *basidiomycete Lactarius vellereus*. From these facts they opined that the system tyrosinase—phenol—amino-acid was a much more complicated one than Happold and Raper thought. According to them the amino-acids played an active part in the system and that no *ortho*-quinone was probably formed.

Kisch and Schuwirth (*Biochem. Z.*, 1931, **242**, 1 ; 1932, **244**, 440 ; 1932, **247**, 371 *et al*) have studied the oxidative deamination of the amino-acids by the catalytic activity of *o*-quinone and some other substances producing *p*-quinone. They have shown that *o*-quinone is highly specific in its action. Quinol, benzoquinone, protocatechuic acid, pyrogallol, phloroglucinol are unable to effect deamination at p_H 6·8 and cause a feeble deamination at p_H 9·12 (*Biochem. Z.*, 1932, **249**, 63). At p_H 9-12 resorcinol is highly active producing 50% of the calculated ammonia from glycine. From the above facts it is evident that the exact mechanism of the deamination of the amino-acids in the system tyrosinase—phenol—amino-acid is yet a disputable point.

Now the mode of action of tyrosinase on phenols can be imitated by sols of tungstic acid and molybdic acid in presence of hydrogen peroxide as shown by the present author in a previous paper (*J. Indian Chem. Soc.*, 1937, **14**, 291). As the system tyrosinase—phenol can bring about the secondary oxidation of the amino-acids, it is expected that the system phenol—sol—H_2O_2 will bring about the same oxidation and it has actually been found to be the case. An attempt is therefore made to throw light on the mechanism of the reaction and the part played by the amino acids.

In this paper the author has made a systematic study of the influence of a wide range of substances on the secondary oxidation of the amino-acids by means of hydrogen proxide in presence of tungstic acid sol. The substances used are phenol, *o*-, *m*-, and *p*-cresols, catechol, resorcinol, quinol, pyrogallol, guaiacol, carvacrol, thymol, phloroglucinol, α- and β-naphthols, thioglycollic acid, tyrosine and gallic acid. The amino-acids used are glycine, alanine, leucine, aspartic acid, glutamic acid and tyrosine. In addition to these, the action of the following quinones, *o*- and *p*-quinones, α-naphthoquinone, *p*-xyloquinone, phenanthraquinone and acenaphthinequinone, on amino-acids without the addition of catalyst and H_2O_2, is also studied.

EXPERIMENTAL.

All the substances taken were chemically pure. Conductivity water was used in the preparation of all aqueous solutions. Either Na_2WO_4, as it is, or tungstic acid sol was used as catalyst. The sol was prepared by the addition of dilue HCl to sodium tungstate by the usual method and its p_H was about 5. Fresh solution of hydrogen peroxide was prepared from Merck's perhydrol. Amino-acids (Pfansteihl) were dissolved in phosphate buffer of p_H 6·5. The experiments were carried out in Pyrex conical flasks kept at room temperature about 25°. Preliminary experiments showed that no oxidation of the amino-acids occurs in the system amino-acid—sol—H_2O_2. Neither any ammonia nor any aldehyde could be detected even after 72 hours. But when a phenol was added to the above system, oxidation of the amino-acid took place. The reaction in the case of glycine may be represented as

$$CH_2(NH_2)\,COOH + O = H{\cdot}CHO + NH_3 + CO_2.$$

The formation of formaldehyde can be easily detected by means of Schryver's reagent, starting with suitable concentration (0·5 g.) of glycine in presence of *p*-cresol.

The reaction mixture consisting of phenol—catalyst—H_2O_2—amino-acid was allowed to stand at room temperature for a period of 24 hours. After that period the total quantity of ammonia in the whole of the reaction mixture was estimated by the method of White-horn as described in the oxidation of tyrosine. The amount of ammonia liberated is indicated by varying number of + ive signs. A negative sign indicates the complete absence of ammonia, + sign signifies "Ammonia easily detectable." The results are given in Table I Strict control was kept for every experiment in which water was added in place of the solution of phenol.

TABLE I.

$H_2O_2 = 45$ mg. $Na_2WO_4 = 0{\cdot}002M$. Total volume = 25 c. c.

Glycine = 50 mg.

Phenols used.	Deamination.	Phenols used.	Deamination.
Phenol (20 mg.)	+ +	Carvacrol (100 mg.) dissolved in minimum quantity of alcohol	+ +
o-Cresol (20 mg.)	+ +	Thymol (100 mg.) dissolved in minimum quantity of alcohol	+ +
m-Cresol (20 mg.)	+ +	α-Naphthol (100 mg.) dissolved in alcohol	+ + +
p-Cresol (20 mg.)	+ + +	β-Naphthol, saturated solution in H_2O (10 c c.)	+ + +
Catechol (50 mg.)	+ + +	Gallic acid (100 mg.) in minimum quantity of alcohol.	+ +
Quinol (50 mg.)	+ +	Thioglycollic acid (100 mg.)	— ve
Resorcinol (50 mg.)	+		
Pyrogallol (50 mg.)	+ + +		
Phloroglucinol (100 mg.)	— ve		
Guaiacol (50 mg.)	+ +		
Tyrosine in HCl brought to a p_H about 4 with pure NaOH — (50 mg.)	—ve		

TABLE I (*contd*-).

Alanine = 60 mg.

Phenols used.	Deamination.	Phenols used.	Deamination
p-Cresol (80 mg.)	+ +	Quinol (100 mg.)	+
Catechol (100 mg.)	+	Resorcinol (100 mg.)	?

Leucine = 70 mg.

p-Cresol (80 mg.)	+ +	Quinol (100 mg.)	+
Catechol (100 mg.)	+	Resorcinol (100 mg)	?

Aspartic acid, saturated solution in phosphate buffer of p_H 6·5 = 10 c.c.

p-Cresol (80 mg.)	+ +	Quinol (100 mg.)	+
Catechol (100 mg.)	+ +	Resorcinol (100 mg.)	Traces.

Glutamic acid-saturated solution in phosphate buffer of p_H 6·5 = 10 c.c.

p-Cresol (80 mg.)	+ + +	Quinol (100 mg.)	+ +
Catechol (100 mg.)	+ +	Resorcinol (100 mg.)	+

Tyrosine dissolved in HCl adjusted to a p_H about 4. = 100mg.

p-Cresol (100 mg.)	+

In Table II is given the action of various quinones on amino-acids in the absence of the sol and H_2O_2. The total quantity of ammonia liberated was estimated after 24 hours by the usual method.

TABLE II.

Glycine = 50 mg.

Quinones.	Deamination
Quinone prepared by the method of Willstätter and Muller	+ + +
p-Quinone sat soln. in H_2O (10 c.c.)	+ + +
p-Xyloquinone sat. soln. in alcohol (10 c.c.)	+ + +
α-Naphthoquinone sat. solution in alcohol (10 c.c.)	+ +
Phenanthraquinone sat. soln. in H_2O (10 c. c.)	+ +
Acenaphthine-quinone sat. soln. in alcohol (10 c.c.)	+ + +

Alanine, sat. soln. in phosphate buffer of p_H 6·3 = 10 c c.

o-Quinone	+ + +
p-Quinone	+ +

Leucine, sat. soln. in phosphate buffer of p_H 6·3 = 10 c.c.

o-Quinone	+ + +
p-Quinone	+ +

The following quantitative experiments were carried out by determining the amino-nitrogen content of the system by means of the macro-form of Van Slyke's appratus. The amino-nitrogen was determined in a small sample (8 c.c.), at the beginning and after 24 hours Strict control was kept for every experiment in which the amino-acid was replaced by buffer and necessary correction was made to the initial and final volumes of amino-nitrogen obtained. No diminution of NH_2-N takes place in the system amino-acid—sol—H_2O_2 even after 72 hours. The results are given in Table III.

TABLE III.

H_2O_2 = 120 mg. Na-tungstate = 0·002*M*. Temp. = 25 . Total vol. = 40 c.c.

Phenols used.	Amino acids.	NH_2-N 0 hr.	NH_2-N 24 hrs.	Loss of NH_2-N.
p-cresol (0·196 g.)	Glycine	9·439 mg.	8·368 mg.	1 071 mg.
	Alanine	9·384	9·009	0·375
	Leucine	9 494	8·611	0·883
Catechol (0·2 g.)	Glycine	9·494	8·584	0·91
	Alanine	8·592	8·270	0·322
	Leucine	7·979	7.229	0·75
Resorcinol (0·2 g.)	Glycine	9·231	8·998	0·233
	Alanine	8·592	8 645	–
	Leucine	7·818	7·025	–
Quinol (0·2 g.)	Glycine	9·139	8·742	0·697
	Alanine	9·022	8·807	0·215
	Leucine	7·979	7·444	0·535
p-Quinone (sat. soln. in H_2O = 10 c.c.)	Glycine	9·558	8·116	1·442
	Alanine	9·314	8·285	1·029
	Leucine	8·989	7.743	1·246

Of the amino-acids, glycine, alanine and leucine, glycine is more readily deaminised than leucine and leucine is more easily deaminised than alanine. The same observation was also made by Robinson and McCance (*Biochem. J.*, 1925, **19**, 251). Of the phenols, *p*-cresol, catechol, quinol, and resorcinol, *p*-cresol is most active, then come catechol, quinol and lastly resorcinol.

From the above tables it is evident that the oxidative deamination of the amino-acids in the secondary system takes place in the presence of all phenols in the primary system.

The following experiments were carried out to show whether the phenols act as catalytic agents in the deamination of the amino-acids by hydrogen peroxide in the absence of the sol. The diminution of the NH_2-N content of the system amino-acid—phenol—H_2O_2 was measured after 24 hours by keeping proper control. The results are given in Table IV.

TABLE IV.

$H_2O_2 = 120$ mg. Temp. = 30 . Total volume = 40 c.c.

Phenols used.	Amino-acids.	NH_2-N in 8 c.c. o hr.	24 hrs.	Loss of NH_2-N
p-Cresol (0·196 g)	Glycine	9·692 mg.	9·692 mg.	—
	Alanine	9·326	9·299	—
	Leucine	9·291	9·238	—
Catechol (0·2 g.)	Glycine	9·318	9·210	0·108 mg.
	Alanine	9·040	8·996	—
	Leucine	9 127	9·154	—
Resorcinol (0·2g.)	Glycine	9·9603	9·4248	0·5355
	Alanine	9 426	9·533	—
	Leucine	9·529	9·689	—
Quinol (0·2g	Glycine	9·5854	9.4248	0·1606
	Alanine	9·132	9·132	—
	Leucine	9·439	9·385	-

DISCUSSION.

On the basis of the experimental results in the oxidation of the amino-acids by the system phenol—tungstic acid—H_2O_2, the deamination of the amino-acids can be explained by the following mechanism of reaction.

The deamination of the amino-acids does not occur by sol and hydrogen peroxide but when a phenol is added, oxidation takes place. As phenols are all oxidised by sol and H_2O_2, so phenol itself or some oxidation product of phenol is responsible for the deamination, or the oxidation of the amino-acids is an induced reaction by the primary system phenol—sol—H_2O_2. It has been observed that though *p*-cresol is most active in causing deamination of the amino-acids in the secondary system, it does not catalyse the oxidation of amino-acids by means of hydrogen peroxide. In the case of catechol and quinol slight amount of ammonia is produced only with glycine (*vide*, Table IV). This slight deamination is probably due to the formation

Should the deamination be due to some oxidation product of resorcinol, the amount of deamination would be reverse to that actually observed.

Now in Table I, we have used a great number of phenolic substances which are likely to produce different quinones and have found that they all cause the deamination of amino-acids. Tyrosine is, however, peculiar in this respect. It is neither deaminised itself during the first few stages of oxidation, as shown in the previous paper, nor cause any external deamination of amino-acids. The mechanism of the oxidation of tyrosine by tyrosinase has been extensively studied by Raper and his school and the absence of deamination has been explained (*cf.* Kar, *J. Indian Chem. Soc.*, 1937, **14**, 271). Tyrosine is deaminised slightly by the system *p*-cresol—sol—H_2O_2, when it is used as an external amino-acid. Schweizer (*Biochem. Z.*, 1917, **78**, 37) also could detect small quantities of ammonia with Nessler's reagent after tyrosine had been acted upon by tyrosinase in presence of *p*-cresol.

In Table II, the action of different quinones on amino-acids are studied and it has been found that they all cause deamination in the absence of sol and hydrogen peroxide.

If the oxidation of the amino-acids be an induced reaction by the primary system, phenol-sol-H_2O_2, the systems tyrosine-sol-H_2O_2, and thioglycollic acid-sol-H_2O_2, would also cause deamination. With both the systems no trace of ammonia could be detected.

From the above facts we can draw the conclusion that the deamination of the amino-acids is not due to the formation of *ortho*-quinone alone in the primary system but due to the formation of all quinones. The amino-acids do not play any active part as Robinson and McCance supposed (*loc. cit.*).

The author wishes to express his indebtedness to Prof. J. C. Ghosh for his unfailing interest and encouragement and for facilities offered.

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Phenols used	Amino-acids	NH$_2$-N in 8 c.c		Loss of NH_2-N
		0 hr.	24 hrs.	
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On the basis of the experimental results in the oxidation of the amino-acids by the system phenol—tungstic acid—H_2O_2, the deamination of the amino-acids can be explained by the following mechanism of reaction.

The deamination of the amino-acids does not occur by sol and hydrogen peroxide but when a phenol is added, oxidation takes place. As phenols are all oxidised by sol and H_2O_2, so phenol itself or some oxidation product of phenol is responsible for the deamination, or the oxidation of the amino-acids is an induced reaction by the primary system phenol—sol—H_2O_2. It has been observed that though *p*-cresol is most active in causing deamination of the amino-acids in the secondary system, it does not catalyse the oxidation of amino-acids by means of hydrogen peroxide. In the case of catechol and quinol slight amount of ammonia is produced only with glycine (*vide*, Table IV). This slight deamination is probably due to the formation of the corresponding quinones by means of hydrogen peroxide, while its absence with *p*-cresol is due to the fact that it is not attacked by hydrogen peroxide alone. The facts with resorcinol are somewhat different. A greater amount of deamination of glycine occurs by means of hydrogen peroxide in presence of resorcinol alone than it does by the system resorcinol—sol—H_2O_2 (*vide*, Tables III and IV). So it is obvious that in the deamination of glycine by hydrogen peroxide, resorcinol itself acts catalytically. Should the deamination be due to some oxidation product of resorcinol, the amount of deamination would be reverse to that actually observed.

Now in Table I, we have used a great number of phenolic substances which are likely to produce different quinones and have found that they all cause the deamination of amino-acids. Tyrosine is, however, peculiar in this respect. It is neither deaminised itself during the first few stages of oxidation, as shown in the previous paper, nor cause any external deamination of amino-acids The mechanism of the oxidation of tyrosine by tyrosinase has been extensively studied by Raper and his school and the absence of deamination has been explained (*cf.* Kar, *J. Indian Chem. Soc*, 1937, **14**, 271). Tyrosine is deaminised slightly by the system *p*-cresol—sol—H_2O_2, when it is used as an external amino-acid. Schweizer (*Biochem. Z.*, 1917, **78**, 37) also could detect small quantities of ammonia with Nessler's reagent after tyrosine had been acted upon by tyrosinase in presence of *p*-cresol.

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STUDIES IN THE COAGULATION OF COLLOIDS. PART XVIII. THE "*ZONAL EFFECT*" AND ANTINORMAL CHANGE OF OPACITY DURING THE *SLOW* COAGULATION OF COLLOID MANGANESE DIOXIDE.

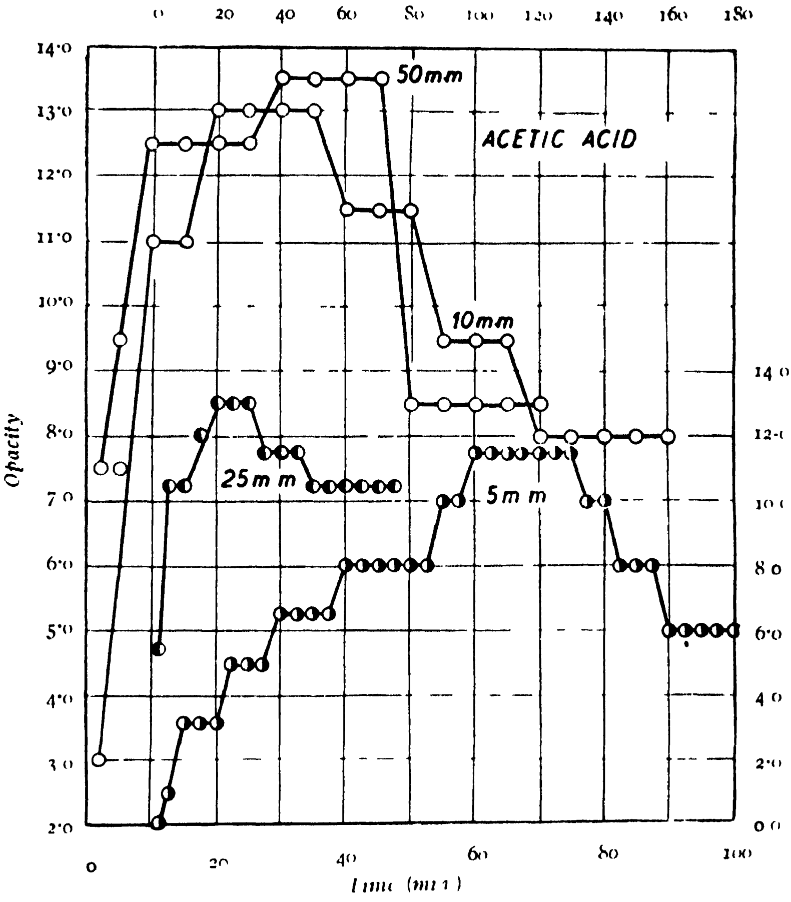
By Shridhar Sarvottam Joshi and P. V. Jagannatha Rao.

In Part XIII of this series (Joshi and S. J. Rao, *J. Indian Chem. Soc.*, 1936, **13**, 311) the obervation was recorded, it would appear for the first time in the field of coagulation kinetics, that during the *slow* electrolytic coagulation of colloid MnO_2, the intensity of light transmitted (measured by means of a sensitive thermopile and Broca galvanometer) diminished '*zonally*', that is, through discontinuities with respect to the coagulation time. Further evidence in this line was obtained by colorimetric measurements of the coagulation of the same sol using mercurous sulphate as the coagulant (Joshi and Purushottam, *Current Science*, 1936, **4**, 870). In view of the obvious bearing of these results on the current theories of the mechanism of coagulation and of its kinetics, it was considered desirable to study this effect in more detail.

EXPERIMENTAL

Colloid manganese dioxide was prepared and its colloid content determined as described in an earlier paper (Joshi and Rao, *J. Indian Chem. Soc.*, 1936, **13**, 217). The last quantity was 1·5 g. of MnO_2 per litre *in the coagulating mixture*. The concentrations of the coagulants employed, *viz.*, solutions of different strengths of acetic acid (Fig. 1, 2), potassium chloride (Fig. 3, 4) and barium chloride (Fig. 5) are expressed in millimols per litre (mm.), also in the *mixture*. The opacity was determined by means of a Duboscq colorimeter as described previously (Joshi and Kulkarni, *ibid.*, 1936, **13**, 441). The variations of opacity during these coagulations are shown graphically in Figs. 1-5; these are selected as typical out of a greater number of curves actually studied, where different origins are employed to prevent overlapping of curves and for economy of space, the appropriate scale units are indicated in the corresponding parts of the diagrams.

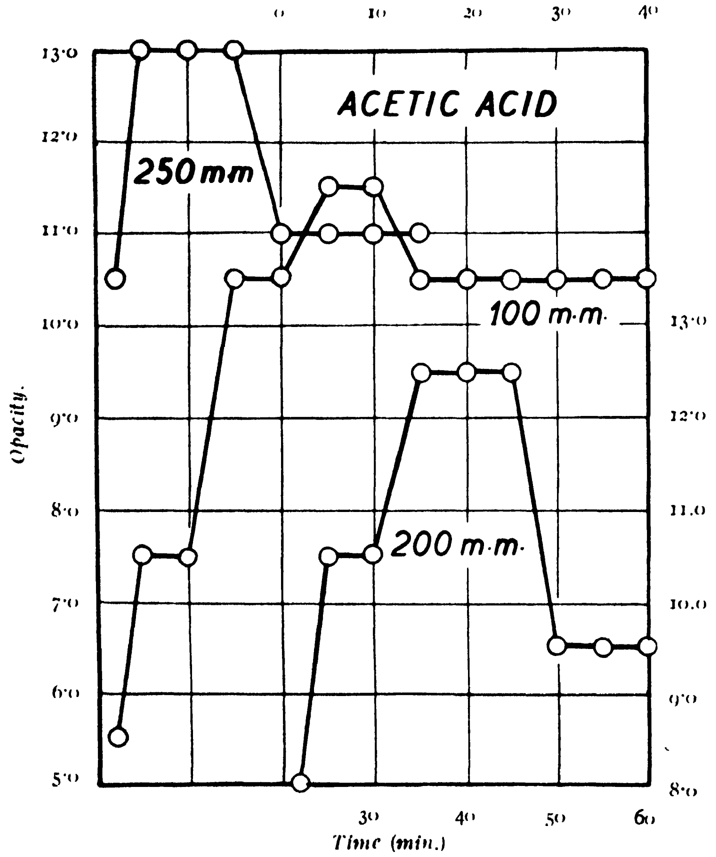
FIG. 1.



DISCUSSION.

From the very beginning of observation of the coagulation phenomena an increase of opacity (turbidity) has been taken by colloid chemists to be in general an index of coagulation. Indeed, this assumption is tacitly implied in numerous quantitative investigations of the kinetics of coagulation. Our results disclose now a remarkable restriction in the generality of the correctness of the above assumption. It is seen that there is the familiar overall increase of opacity during the early stages of coagulation, except when the two lowest concentrations of KCl were employed (*cf.* curves 1, 2, Fig. 3); in these latter coagulations, contrary to the usual experience, the opacity has ***diminished***. It is also interesting to observe that a diminution of opacity is produced subsequent to the initial phase of coagulation which latter is characterised by the familiar rise of opacity. It must be pointed out here that as is customary in these kinetic measurements, the opacity observations were discontinued as soon as the coagulating mixture showed the least sensible production of any optical heterogeneities due to the coagulum. An increase of the particle-size due to micellar coalescence is the chief, if not the only, process constituting coagulation. To this, chiefly, is to be ascribed the familiar rise of opacity of a colloid; other factors also contribute to the effect, *viz.*, increase of opacity, such as the nature of the micellar surface, their average effective shape, number per unit volume, the characteristic optical absorption of the dispersed material and that constituting the continuous medium; their refractivities, optical densities and states of hydration; and lastly, perhaps the electrical charge. These cannot be determined

FIG. 2.



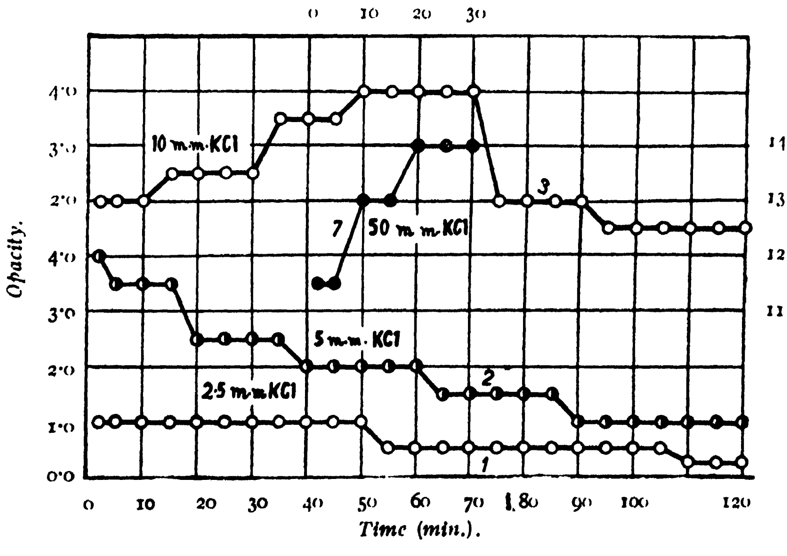
directly to any thing like a satisfactory accuracy. Consequently, except perhaps in the case of a few monodisperse sols, the theory of the optics of a colloid even in the pure state is still largely in an uncertain state, despite notable contributions in the line (for references, *cf.* Joshi and Sarkar, *loc. cit.*). Reference may, however, be made to two deductions of fairly general applicability due to (*i*) Rayleigh (*Phil. Mag.*, 1871, **4**, 107, 274, 447) and (*ii*) Tolman (*cf.* Ware, "Chemistry of the Colloidal State" 2nd Ed., 1936, New York, p. 99). They have obtained respectively, the following expressions for I, the opacity of a colloid of strength c in g. per unit volume :

$I = k.c.d^3$... ... for *small* particles ... ... (*i*)

$I = k_1.c/d$... .. for *large* particles ... ... (*ii*)

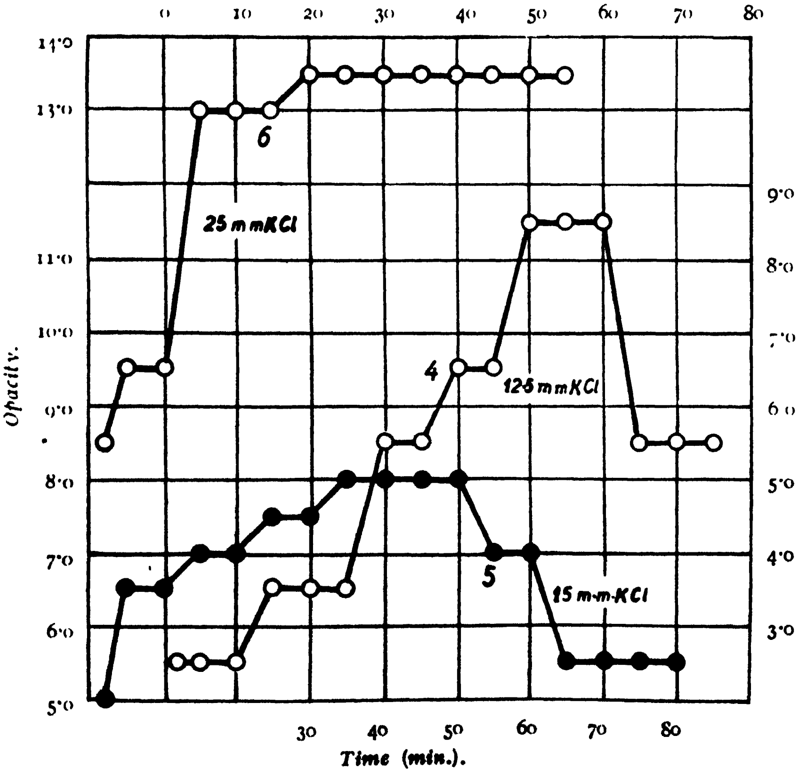
k and k_1 are proportional constants and d, the micellar diameter. It follows from these equations that for a given constant mass of the colloid in two solutions, I, the opacity will increase with an increase of d for small particles in other systems. With large d, I will *diminish* by increase in d. The results of Bechhold and Hebber (*Kolloid Z.*, 1922, **31**, 70) on the opacities of differently sized suspensions of barium sulphate show that I increases progresssively with increase of d over a certain range, *viz.*, 2·5 to 800 $\mu\mu$; thereafter, I diminishes for further increase in d.

FIG. 3.



Our results showing an intial rise and a subsequent fall in opacity during coagulation can, therefore, be, *in part,* ascribed to a progressive increase of the micellar size during coagulation. That some additional factors are involved is shown by the fact when the smallest concentrations of KCl were used (curves 1, 2, Fig. 3) there is instead of a rise of opacity, a *diminution.* On the above considerations, this might suggest perhaps a decrease of the particle-size. This last is by no means unlikely. Considerable evidence is available in the literature that addition of very small amounts of coagulants to a colloid usually imparts an increase in stability, apparently suggestive of a diminution of size. It is, however, not unlikely that this result might also be derived from adsorption of ions carrying a like charge or of the neutral molecules, or what is more likely, of both. It might also come about by diminished hydration. It was emphasised in an earlier paper (Joshi and Kulkarni, *J. Indian Chem. Soc.*, 1936, **13**, 439) that *the opacity of a colloid might be, in part, more than a merely micellar property; it might also arise by a macroscopic, bulk effect of the system as a*

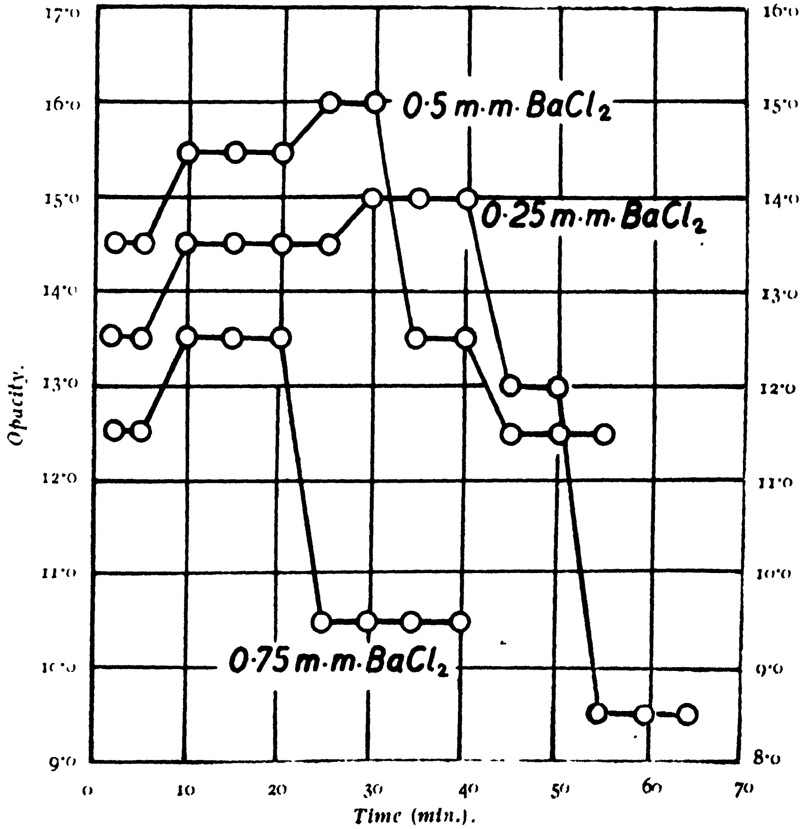
FIG. 4.



whole, that is, by the continuous medium and the dispersed material acting together in a common net-work or a body effect. It was observed that such a postulate was necessary from a consideration of the viscous behaviour of colloids (*loc. cit.*). This gives an additional meaning to the factor of micellar hydration, which is seen to be variable during coagulation. Observation of characteristic facts is needed for suggesting the lines for a theoretical elucidation of the working of the above factors. As such, our result that besides the familiar phase, during which opacity increases by coagulation, there is another, characterised by a *decrease* of this quantity, is interesting.

Another remarkable feature of the foregoing opacity-time curves is that not only the familiar increase of opacity during coagulation, but also its reverse during the latter stage is not time-continuous but *zonal*. By considering the series of curves for different concentrations of a given coagulant

FIG. 5.



(*cf.* especially Figs 1, 2 and 3, 4), it is seen that this *zonal effect* (as indicated by the number of discontinuities in a given section of the coagulation-time curve) is reduced by using very high and very low concentrations of the electrolyte. It is maximum for moderate values. This is fully in agreement with numerous results on the refractometric observations from these laboratories on the *zonal effect* during various coagulations (Joshi and S. J. Rao, *J Indian Chem. Soc.*, 1936, **13**, 141; Joshi and Panikkar, *ibid.*, 1936, **13**, 309; Joshi and N. H. Rao, *ibid.*, 1936, **13**, 775; Joshi and T. M. Menon, *ibid.*, 1937, **14**, 103 ; Joshi and Sarkar, *J. Bombay Univ.*, 1935, **4**, 140 ; Joshi and S. J. Rao, *Kolloid Z.*, 1936, **76**, 145 ; *Fettchem. Umsch.*, 1936, **3**, 36). The earlier results on viscosity changes during numerous *slow* coagulations, from these laboratories have also suggested in the main the same conclusion, that is, discontinuities on viscosity—time curves are least conspicuous during very rapid and very slow coagulations (Joshi and Viswanath, *J. Indian Chem. Soc.*, 1933, **10**, 329; Joshi and Menon, *ibid*, 1933, **10**, 599; Joshi and Nanjappa, *ibid*, 1934, **11**, 133; Joshi and Iyengar, *ibid*, 1934, **11**, 555, 573; Joshi and Panikkar, *ibid.*, 1934, **11**, 797; also, *J. chim. Phys.*, 1935, **32**, 455; *Proc. Acad. Sci. U.P.*, 1935, **5**, 41)

SUMMARY

Results are given for the variation of *I*, the opacity (determined colorimetrically) of colloid MnO_2 when coagulated by differently concentrated solutions of CH_3COOH, KCl and $BaCl_2$. The opacity—time curves show two sections. In the first section *I* increases with time; in the second, the opposite. The last was also observed when but small quantities of the coagulators were employed. Furthermore, during both the stages when *I* showed the familiar increase or otherwise, the change was time-discontinuous or '*zonal*.' In agreement with earlier findings from these laboratories, "*zonal effect*' was most pronounced for *medium* concentrations of the coagulant.

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Received March 22, 1937

OBITUARY

PROF. PANNA LAL.

BORN 1890. DIED 16TH MARCH, 1937.

The Indian Chemical Society has sustained a great loss in the recent death of Prof. Panna Lal who joined the Society as a Fellow in 1926. He was born at Benares in the year 1890, and received his early education at the Central Hindu School of Benares He obtained the B.Sc. degree from the Central Hindu College and the M.Sc. degree in chemistry from the Muir Central College, Allahabad. Soon afterwards he was appointed as a demonstrator in chemistry at St. John's College, Agra. He joined the Patna College as a teacher of chemistry in 1916. He was transferred to the Science College, Patna, when that institution was created in 1927. He held the post of an Assistant Professor of chemistry at the time of his death.

Professor Panna Lal was a man of great personal attraction. He was simple in his habits and amiable in disposition. As a teacher he was loved and respected by his students and colleagues.

Below is given an account of the research work published by Prof. Panna Lal :

1. Panna Lal and N. C. Nag—On the estimation of alcohol in spirituous liquors (*J. Soc. Chem. Ind.*, 1918, **37**, 290).

2. Panna Lal and P. B. Ganguli—Studies on the effect of ultra-violet light on colloids. Part I. (*J. Indian Chem. Soc.*, 1929, **6**, 547).

3. Studies on the effect of ultra-violet light on colloids. Part II. (*ibid.*, 1930, **7**, 573).

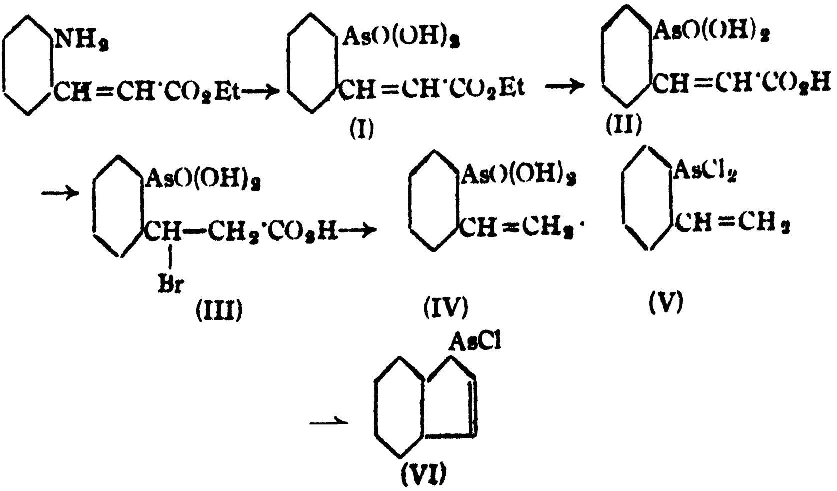
4. Photochemical reduction of ferric salts of organic acids (*Z. anorg. Chem.*, 1936, **229**, 16).

P. B. G.

STUDIES IN ORGANO ARSENIC COMPOUNDS. PART VI. SYNTHESIS OF 1-CHLOROARSINDOLE FROM CINNAMIC ACID.

By Hirendra Nath Das-Gupta.

The present investigation is an attempt to synthesise 1-chloroarsindole by the conversion of *o*-aminocinnamic acid and its ethyl ester into the corresponding arsonic acid which may then be transformed into arsindole by Fischer's method. *o*-Aminocinnamic acid by Bart's reaction gave a tri-derivative (*cf.* Goswami and Das-Gupta, *J. Indian Chem. Soc.*, 1931, **8**, 417) which could not be converted into the corresponding indole derivative under usual conditions. Ethyl *o*-aminocinnamate, however, gave a primary arsonic acid (I) in good yield which can be easily hydrolysed to cinnamic-*o*-arsonic acid (II), but the latter does not give arsindole by Fischer's method. In acetic acid solution (II) reacts with hydrogen bromide to give β-bromohydrocinnamic-*o*-arsonic acid (III). When treated with dilute sodium carbonate the arsonic acid is converted into styrolene-*o*-arsonic acid (IV) (*cf.* Basler, *Ber.*, 1884, **17**, 596, 1494). Reduction of the styrolene compound with sulphur dioxide in hydrochloric acid solution gives styrolene-*o*-arsenious chloride (V), which by Friedel-Crafts' reaction gives 1-chloroarsindole (VI), identified by the formation of mercuric chloride double compound and the picrate and also mixed m.p. with a sample prepared from β-chlorovinylphenylchloroarsine (Das-Gupta, *J. Indian Chem. Soc.*, 1937, **14**, 349).



EXPERIMENTAL.

tris-o-(β-Carboxyvinyl)-phenylarsenic Oxide or tris-Cinnamic-o-arsenic Oxide, $(C_6H_4 \cdot CH{=}CH \cdot COOH)_3AsO$ —The diazo solution from *o*-aminocinnamic acid (5 g.) was added gradually to a well cooled and mechanically stirred mixture of sodium carbonate (12 g.), arsenious acid (4 g.), copper sulphate (15 g.) and water (40 c. c.). The resulting dark brown solution was filtered, concentrated to a low bulk, cooled and filtered again. The filtrate was just acidified with hydrochloric acid and the precipitated dark brown solid was purified from alcohol as yellow amorphous solid not melting up to 300°. [Found: C, 60·1; H, 3·6; As, 13·8 $C_{27}H_{21}O_7As$ requires C, 60·9; H, 3·9; As, 14·3 per cent).

o-(β-Carbethoxyvinyl) phenylarsonic Acid (I).—To mechanically stirred and cooled solution of anhydrous sodium carbonate (75 g.), arsenious oxide (30 g.), copper sulphate (1 g.) and water (150 c c), the diazo solution prepared from *o*-aminocinnamic ester (15 g.), hydrochloric acid (24 c.c), water (50 c.c.) and sodium nitrite (9 g.) was added. Too much frothing occurred but this was controlled by increasing the speed of rotation of the stirrer. The solution was stirred for 1 hour more and allowed to remain overnight, filtered and one third of the filtrate was taken and the acid was precipitated by concentrated hydrochloric acid avoiding excess. The precipitated dull yellow solid was separated, dried, and then purified three times from methyl alcohol and ether. It is a brownish yellow product sintering at 175° but not melting up to 360°. [Found: C, 43·8; H, 4·1; As, 25·2. $C_{11}H_{13}O_5As$ requires C, 44·0; H, 4·3; As, 25·0 per cent].

o-(β-Carboxyvinyl)-phenylarsonic Acid (II).— The remaining filtrate from the above procedure was first heated under reflux to hydrolyse the ester and then concentrated to a low bulk, cooled and filtered. The filtrate on acidification gave a dull yellow mass. This was crystallised from methyl alcohol and ether as golden yellow amorphous powder, m.p. 205-6°. The acid is readily soluble in alcohol, acetic acid, and hot nitrobenzene, moderately soluble in water and chloroform and insoluble in benzene, ether, carbon disulphide and carbon tetrachloride. (Found: C, 39·8; H, 2·9; As, 27·4. $C_9H_9O_5As$ requires C, 39·7; H, 3·3; As 27·5 per cent.).

β-Bromohydrocinnamic-o-arsonic Acid (III)—*o*-(β-Carboxyvinyl)-phenylarsonic acid (7 g.) and glacial acetic acid (50 c.c.), saturated at 0° with anhydrous hydrogen bromide, were heated in a sealed tube at 100° for ½ hour and the pressure released at once with a view to prevent the action of excess of hydrogen bromide on the addition product. The reaction mixture was heated for 10 minutes on a water-bath and diluted with water in the cold ; the yellow product separating was taken up in chloroform, filtered and precipitated by ether. It was then crystallised from dilute acetic acid as a yellow compound, m.p. 185°. (Found: Br, 21·9; As, 21·2. $C_9H_{10}O_5BrAs$ requires Br, 22·6; As, 21·2 per cent). It is soluble in alcohol, chloroform and acetic acid ; sparingly soluble in benzene, carbon disulphide, and insoluble in ether and carbon tetrachloride.

Styrolene-o-arsonic Acid (IV).—β-Bromohydrocinnamic-*o*-arsonic acid was heated under reflux with a solution of sodium carbonate (5 % excess of theoretical quantity) for 1 hour, filtered and then acidified after cooling. A yellow precipitate was obtained which was crystallised from alcohol as a yellow powder, m.p. 150°. (Found: C, 41·8; H, 3·8; As, 32·7. $C_8H_9O_3$ As requires C, 42·1; H, 3·9; As, 32·8 per cent).

Styrolene-o-arsenious Chloride (V).—Syrolene-*o*-arsonic acid was dissolved in alcohol and excess of concentrated hydrochloric acid was added. The solution was first warmed and then saturated with sulphur dioxide for ½ hour in the presence of a crystal of potassium iodide. The major portion of the alcohol was removed and the residue dried on a porous plate and then crystallised from carbon disulphide as a yellow amorphous powder, m.p. 55°. (Found: C, 38·2; H, 2·6; Cl, 28·4; As, 30·1. $C_8H_7Cl_2As$ requires C, 38·5; H, 2·8; Cl, 28·5 ;As, 30·1 per cent).

1-*Chloroarsindole* (VI).—Styrolene-*o*-arsenious chloride (7 g.) and anhydrous aluminium chloride (3 g.) in absolute carbon disulphide (300 c.c.) were heated under reflux. The heating was continued for about 5 hours. The mass was decomposed by ice-cold dilute hydrochloric acid and extracted several times with carbon disulphide. The extract was of brown colour and contained a brownish violet solid giving fluorescence in alcohol. It was filtered and the solvent evaporated off in an inert atmosphere. The residual brown oil, having a very painful penetrating odour was distilled in *vacuo* at 125-30°/5 mm. The colour of the yellow oil became dark on keeping. The mercuric chloride addition product of its methyl derivative melted at 151° and was found to be identical with hat described before (Das-Gupta, *loc. cit.*). (Found : Cl, 16·5 ; As, 35·1. C_8H_6ClAs requires Cl, 16·7 ; As, 35·2 per cent).

My grateful thanks are due to Dr. M. N. Goswami and to Mr. B. C. Ray for their keen interest throughout this investigation.

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STUDIES IN ORGANO-ARSENIC COMPOUNDS. PART VII. SYNTHESIS OF ARSINDOLE DERIVATIVES.

By Hirendra Nath Das-Gupta.

The present communication deals with the various attempts to prepare arsindole derivatives from ω-bromostyrene. The principal aim was to prepare a primary arsine like β-phenylvinyldichloroarsine which would produce arsindole derivatives by the application of the Friedel-Crafts' reaction (*cf.* Burrows and Turner, *J Chem Soc.*, 1921, **119**, 430).

The suitable intermediate compound for the preparation of β-phenylvinyldichloroarsine from ω-bromostyrene is either the arsonic acid, or a mercury derivative of the type $[(Ph\ CH=CH)_2Hg]$. The yield of the arsonic acid from the styrene by Meyer's reaction (*Ber*, 1883, **16**, 1440) is very poor, due probably to the remarkable stability of the ω-bromostyrene in alkaline solution and its tendency to produce phenylacetylene and ethoxyphenylethane in alcoholic caustic alkali Attempts at converting the sodium salt of the arsenic acid to the corresponding dihalide proved futile as it readily undergoes decomposition in acid medium giving arsenious acid. This behaviour is found to be analogous to that of benzylarsonic acid with hydrochloric acid.

The mercury derivative of styrene has been prepared by the two well known methods, *viz.*, (*i*) sodium amalgam method and (*ii*) by reacting the bromide with metallic sodium and mercuric chloride The yield by the former process is very poor, whilst the latter method gives a better yield of mercury distyrene and a small quantity of styrene-mercuric bromide Mercury distyrene when treated with arsenic trichloride yielded not the dihalogen derivative but mercuric chloride and non-arsenated derivative.

Burrows and Turner (*loc cit*) have been able to isolate Ph(Me)AsI by simply allowing phenyldichloroarsine in alcohol to react with methyl iodide and sodium hydroxide. The reaction product after acidification with hydrochloric acid and saturation with sulphur dioxide gave the arsine.

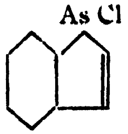
ω Bromostyrene when treated with alcoholic phenyldichloroarsine in presence of alkali (*cf* Burrows and Turner, *loc. cit.*) gave a small yield of the impure bromoarsine, which during purification by distillation under reduced pressure gave a yellow viscous mass identified to be 1-phenylarsindole.

All attempts in the above directions having proved unsuccessful attention was directed towards the preparation of different arsines from ω-bromostyrene by the adoption of the methods applicable to aromatic halides.

(*i*) ω-Bromostyrene was subjected to Fittig's reaction and a tertiary arsine was obtained along with small quantities of both primary and secondary arsines. The tertiary arsine on treatment with excess of arsenic trichloride at a high temperature (*cf.* Michaelis and Rees, *Ber.*, 1882, **15**, 2876) gave 1-chloroarsindole through the intermediate unstable compound, $PhCH = CHAsCl_2$.

$$3PhCH : CHBr + 6Na + AsCl_3 \longrightarrow (PhCH : CH)_3As + 6\,NaCl$$

$$(PhCH : CH)_3As + 2AsCl_3 \longrightarrow \underset{\text{(unstable}}{3PhCH : CH{\cdot}AsCl_2} \longrightarrow$$

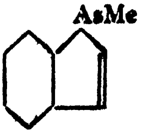


(*ii*) β-Phenylvinyldimethylarsine ($PhCH = CHAsMe_2$) was prepared from ω-bromostyrene and cacodyl bromide. The arsine was treated with chlorine to get the quinquevalent compound which was decomposed by heat. In this case also the reaction product was not a compound of the type $PhCH = CHAs(Cl)\,Me$ but the ring-closure took place with the formation of 1-methylarsindole thus :—

$$Ph\,CH = CHBr + 2Na + BrAsMe_2 \longrightarrow PhCH = CH{\cdot}AsMe_2 + 2NaBr$$

$$Ph\,CH = CH{\cdot}AsMe_2 + Cl_2 \longrightarrow Ph\,CH = CH{\cdot}AsMe_2Cl_2$$

$$\xrightarrow{\text{heat}} \underset{\text{(unstable)}}{Ph\,CH = CH{\cdot}As\,(Cl)Me} \longrightarrow$$



(*iii*) The Grignard reaction is also available for the preparation of tertiary arsines, but by this method both the primary and secondary arsines are formed in appreciable quantities along with other by-products

The Grignard reagent from ω-bromostyrene was treated with cacodyl bromide and as expected, a poor yield of β-phenylvinyldimethylarsine was obtained along with styrolene, 1:4-diphenylbutadiene, etc. In a similar way phenylmethyliodoarsine was allowed to react with the magnesium compound from ω-bromostyrene but in this case no reaction took place, the arsine distilled over unchanged and 1:4-diphenylbutadiene could only be isolated.

EXPERIMENTAL.

β-Phenylvinylarsonic Acid.—A solution of ω-bromostyrene (12 g.) in alcohol was added to an alcoholic solution of sodium arsenite (30 g. of arsenious acid in 40 g of sodium hydroxide) and after standing for 24 hours the whole was heated under reflux with constant stirring for 48 hours. The oily layer was extracted with ether and the turbid aqueous layer was diluted with alcohol and allowed to stand overnight. The crystalline solid separating was filtered off, dissolved in water and reprecipitated by alcohol as needle-shaped crystals, yield of the sodium salt being 3·5 g. (Found As, 26·9. $C_8H_7O_3As\ Na_2$ requires As, 27·5 per cent). The alkaline mother liquor was neutralised with glacial acetic acid, filtered from the precipitated solids and the filtrate treated with a saturated solution of barium chloride and kept overnight. The precipitated barium salt (1 g) crystallised from hot water. The free acid was isolated by treating the aqueous alcoholic solution of the sodium salt with the theoretical quantity of dilute hydrochloric acid and by fractional crystallisation.

Mercury Distyrene [$(Ph\ CH = CH)_2Hg$].—(i) A mixture of ω-bromostyrene (18 g.), mercuric chloride (28 g), sodium (5 g.) and dry benzene (60 c.c.) was kept overnight at room temperature. It was then heated under reflux on a water-bath for 8 hours and extracted several times with chloroform and the combined extracts precipitated with ether. The yellow precipitate was crystallised from chloroform, m.p. 150°. It is soluble in chloroform, acetone, sparingly soluble in benzene. It is not acted on by dilute alkali even on boiling. (Found Hg, 49·3, 49·18. $C_{16}H_{14}Hg$ requires Hg, 49·2 per cent).

(ii) A mixture of ω-bromostyrene (10 g.), sodium amalgam (7·5%, 40 g.) and dry xylene (30 c.c.) and ethyl acetate, distilled over phosphorus pentoxide (5 c.c.), was heated under reflux for 7 hours at 140°. The reaction product was separated from the metallic mercury and the solvent evaporated off and the unchanged styrene was removed at 120°/3 mm. The residue was washed with excess of ether and finally extracted with chloroform. From the chloroform extract the mercury derivative was isolated as above, m.p. and mixed m.p. 150°. (Found : Hg, 49·09. $C_{16}H_{14}Hg$ requires Hg, 49·2 per cent).

Styrolene-mercuric Bromide.—The solid left after extraction with chloroform in the above process was washed with excess of alcohol and then with water and the residue was dried in *vacuo*. It is insoluble in the common organic solvents and gives a black precipitate with pyridine. It does not melt up to 330°. (Found : Hg, 51·9. C_8H_7BrHg requires Hg, 52·2 per cent).

Fittig's Reaction with ω-Bromostyrene.

tris-β-Phenylvinylarsine [(Ph CH = CH)$_3$ As].—Sodium (10·5 g.) in the form of wire was taken in a round-bottomed flask provided with an upright condenser and a dropping funnel and allowed to remain for 1 hour in dry benzene (100 c.c.) containing 3 c.c. of ethyl acetate. A mixture of ω-bromostyrene (42 g.) and arsenious chloride (18 g.) was introduced into it. In about 20 minutes the reaction became vigorous and the reaction was controlled by alternately immersing the flask in ice-cold water and water at ordinary temperature and finally it was heated on a water-bath for 1 hour more and allowed to stand for 12 hours. The resulting brown viscous mass was repeatedly extracted with benzene and the solvent evaporated off under reduced pressure. The excess of styrene was distilled at 89-90°/3 mm. The product in the distilling flask solidified to a hard mass on cooling which was dissolved in hot benzene and the solution on concentration gave crystals of arsine, which were recrystallised from methyl alcohol in needle-shaped crystals, m.p. 82°. It is extremely soluble in benzene, toluene, carbon disulphide; soluble in ether, carbon tetrachloride, nitrobenzene, ethyl acetate and is soluble in hot acetic acid, methyl and ethyl alcohol; picrate, m.p. 100°. (Found : C, 74·6 ; H, 5·2 ; As, 19·2. $C_{24}H_{21}As$ requires C, 75·0 ; H, 5·4 ; As, 19·5 per cent).

β-Phenylvinyldimethylarsine, [Ph CH = CH·AsMe$_2$] was prepared in a similar way as the previous compound starting from ω-bromostyrene (36 g.), sodium (9·2 g.), cacodyl bromide (86 g.), dry benzene (200 c.c.) and ethyl acetate (3 c.c.). The reaction was not so vigorous as the previous one and no cooling was necessary and the reaction was completed by heating the mixture for 5 hours on a water-bath. The reaction product was extracted with ether, solvent evaporated off and the viscous oil was distilled at 125-35°/5 mm. It is a yellow oil possessing an offensive odour. (Found : C, 57·1 ; H, 5·9 ; As, 35·9. $C_{10}H_{13}As$ requires C, 57·6 ; H, 6·2 ; As, 36·05 per cent).

Grignard Reaction with ω-Bromostyrene.—ω-Bromostyrene (9 g.) reacted with magnesium (1·2 g.) in dry ether (100 c.c.) in presence of methyl iodide and a crystal of iodine. The last trace of magnesium was dissolved by heating the whole for 1 hour on a water-bath. Cacodyl bromide (9 g.) in ether (20 c.c.) was added drop by drop. After the addition was complete the reaction product was heated on a water-bath for 3 hours. After decomposition by cold dilute hydrochloric acid, the ethereal layer was removed and the aqueous layer extracted several times with ether. On evaporation of the solvent an oil was obtained which on fractionation gave (*i*) up to 65°/5mm., mainly cacodyl bromide, (*ii*) and an oil at 125-140°/5 mm. The solid residue in the flask on crystallisation from alcohol gave shining plates (arsenic-free), m.p. 135°. The second fraction was redistilled at 125-35°/5 mm. (Found : As, 35·7. $C_{10}H_{13}As$ requires As, 36·05 per cent).

β-Phenylvinyltrimethylarsonium Iodide, [PhCH = CHAsMe$_3$I], prepared by heating β-phenylvinyldimethylarsine with excess of methyl iodide, separated as a yellow solid. It was washed with ether and dissolved in chloroform. The chloroform extract was concentrated and poured into ice-cold ether when needles were obtained, m.p. 155°. It is very soluble in methyl alcohol, chloroform, sparingly in carbon disulphide and insoluble in benzene, ether and petroleum ether. (Found : As, 21·1. $C_{11}H_{16}IAs$ requires As, 21·4 per cent).

Mercuric Chloride Double Salt [Ph CH = CH·AsMe$_2$, HgCl$_2$].—Ethereal solutions of mercuric chloride and β-phenylvinyldimethylarsine in molecular proportions were mixed together and the precipitated solid was dissolved in chloroform and reprecipitated by ether, the operation being repeated several times. Finally it was crystallised from chloroform, m.p. 131°. (Found : Hg, 41·5. $C_{10}H_{13}As\,Hg$ requires Hg, 41·7 per cent).

tris-β-Phenylvinylmethylquaternary Arsonium Iodide, (PhCH =CH)$_3$ AsMeI was crystallised from alcohol as needles, m.p. 95°. (Found : As, 14·2. $C_{25}H_{24}I\,As$ requires As, 14·2 per cent).

Synthesis of Arsindole Derivatives.

1-Chloroarsindole.—tris-β-Phenylvinylarsine (10 g.) and arsenic trichloride (35 c.c.) were heated for 7 hours at 180°. The reaction product was treated with excess of 20% hydrochloric acid and the oil obtained was dissolved in excess of ether, the ethereal solution washed with dilute hydrochloric acid, and dried over calcium chloride. The ether was evaporated off in an atmosphere of carbon dioxide and the oil distilled at 120-35°/5mm. as a light yellow oil with a very irritating odour. [Found : As, 35·3 ; M.W. (cryoscopic in benzene), 216·3. C_8H_6Cl As requires As, 35·2 per cent. M.W., 212·5].

It was identified as 1-chloroarsindole by its methyl derivative (*cf.* Das-Gupta, *J. Indian Chem. Soc.*, 1937, **14**, 354) and mercuric chloride double salt of the methyl derivative, m.p. and mixed m.p. 151°.

1-*Methylarsindole*.—A solution of β-phenylvinyldimethylarsine in dry carbon tetrachloride was saturated with dry chlorine. The solvent was removed under reduced pressure and the remaining mass was gradually heated to 185-90°. Decomposition took place with evolution of methyl chloride, volatile chloroarsines, etc. The product was washed with dilute hydrochloric acid and then extracted with ether, the solvent removed and the oil distilled at 138-48°/5 mm. This was redistilled at 140-45°/5 mm. as a golden yellow oil. The mercuric chloride addition product melted at 151°. [Found : As, 39·1 ; M.W. (cryoscopic in benzene), 190·5. C_9H_9As requires As, 39·06 per cent. M.W., 192).

1-*Phenylarsindole*.—A mixture of phenylarsenious chloride (9 g.) and ω-bromostyrene was allowed to stand for 24 hours with caustic soda solution (10 g. in 20 c.c. of water) at room temperature. It was then heated for 10 hours. The mixture was filtered through glass wool and the unaltered oil separated and the aqueous layer acidified with excess of hydrochloric acid in presence of alcohol. The solution was then saturated with sulphur dioxide, when a brown oil separated which was distilled at 165-76°/3 mm. as a brown oil. It was redistilled at 165-70°/3 mm. [Found : As, 29·6 ; M.W. (cryoscopic), 251. $C_{14}H_{11}As$ requires As, 29·5 per cent. M.W., 254].

My grateful thanks are due to Dr. M. N. Goswami and to Mr. B. C. Ray for their keen interest.

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CONDENSATION OF SUCCINIC ANHYDRIDE WITH THE METHYL ETHERS OF DIHYDRIC PHENOLS.

By G. A. Dalal and K. S. Nargund.

Succinic anhydride has been condensed with anisole and the methyl ethers of isomeric cresols by Friedel and Crafts' method (Rosenmund and Schapiro, *Arch, Pharm.*, 1934, **272**, 313). Hostmann (*Chem. Zentil.*, 1896, **II**, 663) obtained a dimethoxybenzoylpropionic acid from the condensation of succinic anhydride with resorcinol dimethylether, while Mitter and De (*J Indian Chem. Soc*, 1935, **12**, 747) obtained β-3:4-dimethoxybenzoylpropionic acid by the condensation of succinic anhydride with veratrole. But in both these cases the reaction does not seem to have been studied thoroughly by using different solvents. We have now condensed succinic anhydride with the mono- as well as dimethyl ethers of dihydric phenols by Friedel and Crafts' method using different solvents and the results obtained are given in the following table.

Methyl ether used	Product obtained	Yield of the product in different solvents.
Veratrole	β-3:4-Dimethoxybenzoylpropionic acid	44% in nitrobenzene. 46 in carbon disulphide 64 in acetylene tetrachloride
Guaiacol	Did not condense under any conditions	
Resorcinol dimethyl ether	β-2:4-Dimethoxybenzoylpropionic acid	88 in nitrobenzene. 50 in carbon disulphide. 60 in acetylene tetrachloride.
Resorcinol monomethyl ether	β-2-Hydroxy-4-methoxybenzoylpropionic acid	40 in nitrobenzene. 35 in carbon disulphide. 40 in acetylene tetrachloride.
Hydroquinone dimethyl ether	β-2:5-Dimethoxybenzoylpropionic acid	70 in nitrobenzene. 40 in carbon disulphide. 45 in acetylene tetrachloride.
Hydroquinone monomethyl ether	Did not condense under any conditions	

The constitution of the product obtained from veratrole was established by oxidation to veratric acid. The product from resorcinol dimethyl ether could not be oxidised by either alkaline potassium permanganate or sodium hypochlorite to any dimethoxybenzoic acid. Its constitution was, therefore, established by its synthesis by the action of succinic anhydride on the Grignard reagent prepared from 4-iodoresorcinol dimethyl ether. The constitution of the product from resorcinol monomethyl ether follows from the fact that on methylation with dimethyl sulphate and caustic soda it gives a product, identical with the one obtained by the condensation of resorcinol dimethyl ether and succinic anhydride. That the side-chain $-COCH_2CH_2COOH$ is in *ortho*-position to the hydroxyl group is inferred from its colour reactions with ferric chloride in which behaviour it resembles 2-hydroxy-4-methoxybenzoic acid. The constitution of the product from hydroquinone dimethyl ether could not be established by its oxidation to dimethyl gentisic acid. Its constitution was, therefore, established by its synthesis by the action of succinic anhydride on the Grignard reagent prepared from bromohydroquinone dimethyl ether.

EXPERIMENTAL.

General Procedure followed for the Condensation of Succinic Anhydride with the Methyl ethers.—Anhydrous aluminium chloride (28 g.) was added in four lots to succinic anhydride (1·2 mol.), the methyl ether (1·2 mol.) and the solvent (100 c.c.) in a round-bottomed flask. Care was taken to see that the temperature did not rise higher than 40°. It was kept at ordinary temperature for 4 hours, decomposed by the addition of ice and hydrochloric acid and distilled with steam to remove the solvent. The solid obtained on cooling was filtered and washed with water. It was then extracted with dilute solution of sodium carbonate, the extract was boiled with the addition of animal charcoal, filtered and acidified. The substance thus obtained was filtered, washed and dried.

β-3:4-Dimethoxybenzoylpropionic acid, m.p. 162°, is soluble in alcohol and acetic acid; slightly soluble in methyl alcohol and chloroform; insoluble in petrol and benzene. Calcium and barium salts are soluble in water and the silver salt soluble in hot water. (Found: C, 60·35; H, 5·95. $C_{12}H_{14}O_5$ requires C, 60·50; H, 5·88 per cent).

Oxidation of the Above Acid.—To the above acid (1 g.) dissolved in a few c.c. of dilute solution of sodium hydroxide, potassium permanganate

(1·2 g.) in 40 c.c. of water was added. The oxidation was complete in half an hour at ordinary temperature. The precipitated MnO_2 was filtered and the filtrate concentrated and acidified. The substance obtained had m.p. 179° and did not depress the m.p. of an authentic specimen of veratric acid.

The *methyl ester* is soluble in the usual organic solvents and crystallises from dilute acetic acid, m.p. 90°. (Found : C, 61·75 ; H, 6·30. $C_{13}H_{16}O_5$ requires C, 61·90; H, 6·34 per cent).

The *ethyl ester* was crystallised from dilute alcohol, m.p. 70°. (Found C, 63·10, H, 6·82. $C_{14}H_{18}O_5$ requires C, 63·16 ; H, 6·77 per cent).

The *semicarbazone* was a white granular powder, m.p. 180°, soluble in hot water. (Found : N, 13·94. $C_{13}H_{17}O_5N_3$ requires N, 14·24 per cent).

β-2:4 Dimethoxybenzoylpropionic acid, m.p. 148°, is soluble in methyl and ethyl alcohol, chloroform, ethyl acetate, acetic acid and hot water. Calcium and barium salts are soluble in water. The silver and lead salts are soluble in hot water. (Found · C, 60·29 ; H, 5·93. Equiv., 236·6 $C_{12}H_{14}O_5$ requires C, 60·50 ; H, 5·88 per cent. Equiv., 238·0).

Synthesis of β-2.4-Dimethoxybenzoylpropionic Acid.—To a boiling suspension of succinic anhydride (5 g.) in benzene (50 c.c) was added the Grignard reagent, prepared from 4-iodoresorcinol dimethyl ether (11 g.) (Kauffmann and Kieser, *Ber.*, 1912, **45**, 2334), magnesium (1·2 g.) and dry ether (50 c.c). It was warmed on a water-bath for 15 minutes, decomposed by ice and dilute sulphuric acid. The benzene-ether layer was extracted with dilute solution of sodium carbonate. The sodium carbonate extract on acidification melted at 135°. It has equivalent wt., 237·0 and forms a silver salt soluble in hot water. The mixed m.p. with the product from resorcinol dimethyl ether was 147°. The m.p. of the synthetic product could not be raised by recrystallisation.

The *methyl ester* was a colourless liquid, b.p. 210°/27 mm. ; n_D^{30}=1·54224. (Found . C, 61·82 ; H, 6·37. $C_{13}H_{16}O_5$ requires C, 61·90 ; H, 6·34 per cent).

The *ethyl ester* was a colourless solid, m.p. 70°, soluble in the usual organic solvents but insoluble in petrol. (Found : C, 63·07 ; H, 6·90. $C_{14}H_{18}O_5$ requires C, 63·16 ; H, 6·77 per cent).

The *semicarbazone* melted at 160°. (Found : N, 14·10. $C_{15}H_{17}O_5N_3$ requires N, 14·24 per cent).

β-5-Bromo-2:4-dimethoxybenzoylpropionic acid, prepared by brominating the parent acid in aqueous solution, had m.p. 178°. It is soluble in hot ethyl alcohol and acetic acid and insoluble in petrol, benzene and chloroform. (Found : Br, 25·15; Equiv., 321·0. $C_{12}H_{13}O_5Br$ requires Br, 25·13 per cent. Equiv., 317·0).

β-5-Nitro-2:4-dimethoxybenzoylpropionic acid, prepared by nitrating the parent acid in glacial acetic acid, had m. p. 173°. It is soluble in hot water, hot methyl and ethyl alcohols and insoluble in chloroform, petrol and benzene. (Found : N, 4·78 ; Equiv., 281·3. $C_{12}H_{13}O_7N$ requires N, 4·95 per cent. Equiv., 283·0).

β-2-Hydroxy-4-methoxybenzoylpropionic acid, prepared by the condensation of succinic anhydride with resorcinol monomethyl ether, is soluble in hot organic solvents and hot water. It crystallises in fine needles from methyl alcohol, m. p. 156°. Calcium and barium salts are soluble in water and the silver salt insoluble in water. (Found : C, 58·72 ; H, 5·45. Equiv., 226·0. $C_{11}H_{12}O_5$ requires C, 58·94 ; H, 5·36 per cent. Equiv., 224·0).

The *methyl ester* is a colourless solid (needles from dilute alcohol), m. p. 85°, soluble in the usual solvents but insoluble in petrol. (Found : C, 60·30 ; H, 5·80. $C_{12}H_{14}O_5$ requires C, 60·50 ; H, 5·88 per cent).

The *ethyl ester*, m. p. 68°, has similar solubilities as the methyl ester. (Found: C, 61·78 ; H, 6·50. $C_{13}H_{16}O_5$ requires C, 61·90 ; H, 6·35 per cent).

The *semicarbazone* is a white granular powder, m. p. 175°, insoluble in all solvents. (Found : N, 14·73. $C_{12}H_{15}O_5N_3$ requires N, 14·94 per cent).

Methylation of-β-2-Hydroxy-4-methoxybenzoylpropionic Acid.—The acid (2 g.), dissolved in 10 c.c. of 10 % solution of sodium hydroxide, was treated with 2 c.c. of dimethyl sulphate and left overnight. It was again treated with the same quantities of dimethyl sulphate and sodium hydroxide and was warmed on a water-bath, cooled and acidified. The substance, m. p. 148°, did not depress the m. p. of β-2:4-dimethoxybenzoylpropionic acid.

β-2:5-Dimethoxybenzoylpropionic acid, m. p. 107° (prisms from acetic acid) is soluble in hot methyl and ethyl alcohol and hot water, insoluble in petrol, chloroform and benzene. Calcium and barium salts are soluble in water and the silver salt soluble in hot water (Found : C, 60·28 ; H 5·82. Equiv., 240·0. $C_{12}H_{14}O_5$ requires C, 60·50 : H, 5·88 per cent. Equiv., 238·0).

β-2:*5-Dimethoxybenzoylpropionic acid* was prepared from bromohydroquinone dimethylether (Noelting and Werner, *Ber.*, 1890, **23**, 3250).

The *methyl ester* crystallised from hot petrol in square plates, m.p. 54°. (Found : C, 61·83 ; H, 6·45 $C_{13}H_{16}O_5$ requires C, 61·90 ; H, 6·34 per cent).

The *ethyl ester* crystallised from dilute alcohol in needles, m.p. 46°. (Found : C, 63·06 ; H, 6·82. $C_{14}H_{18}O_5$ requires C, 63·16 ; H, 6·77 per cent).

The *semicarbazone* crystallised from methyl alcohol, m.p. 195°. It is insoluble in ethyl acetate, benzene, acetic acid, petrol and chloroform. (Found : N, 13·93. $C_{13}H_{17}O_5N_3$ requires N, 14·24 per cent).

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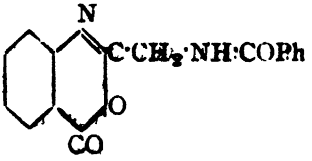
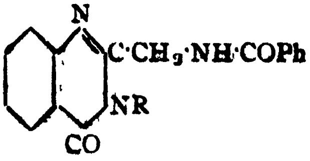
QUINAZOLINES. PART I.

By Tejendra Nath Ghosh.

In a previous communication (Ghosh, *J. Indian Chem. Soc.*, 1937, 14, 124) the synthesis of the oxazine derivative (I) has been described. When heated with an aromatic amine at 160-170°, in presence of copper powder (*cf.* Narang and Rây, *J. Chem Soc.*, 1931, 976), the compound (I) furnishes the quinazoline (II). In this connection, reference is made to the synthesis of quinazolines by heating acetoanthranil with various amines (Anschütz, Schmidt and Greiffenberg, *Ber.*, 1902, 35, 3482; Bogert and Beal, *J. Amer. Chem Soc*, 1912, 34, 516, *and subsequent papers*).



(I)



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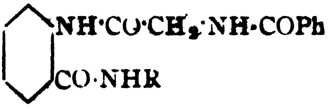

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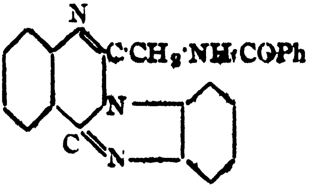

(IV)

When boiled with concentrated hydrochloric acid, the compound (II; R = Ph) yields a mixture of hippuric acid and *o*-aminobenzanilide (*cf.* Bogert and Seil, *J. Amer. Chem. Soc.*, 1906, 28, 890). In order to study the cyclisation of the compound (III) to (II), the hydrolysis of the compound (I) was tried, so that the corresponding acid could be utilised for the preparation of (III). The acid from (I), however, could not be obtained, because, as soon as it is liberated from the sodium salt by acid, it at once passes into (I).

For obvious pharmacological reasons, it seemed of considerable interest to synthesise a compound of the type (IV), in which an imidazole ring is fused with the quinazoline residue. When heated with *o*-phenylenediamine at 170-180° in presence of copper powder, the compound (I) yields (IV) with the elimination of two molecules of water (*cf.* Bistrzycki and Fässler, *Helv. Chim. Acta*, 1923, 6, 525; Späth and Platzer, *Ber.*, 1936, 69, 255).

The compound (IV) is stable towards concentrated hydrochloric acid and forms a hydrochloride.

It has been observed that, although the oxazine derivative (I) readily condenses with aldehydes in presence of acetic anhydride and fused sodium acetate (Ghosh, *loc. cit.*), the quinazolines (II) and (IV) do not lend their apparently reactive methylene groups for condensation with aldehydes under similar conditions. In both cases, some steric influence may be responsible for this inactivity.

EXPERIMENTAL.

4-Keto-2-benzoylaminomethyl-3-phenyl-3:4-dihydroquinazoline (II, R = Ph).—An intimate mixture of the compound (I, 5·6 g.) and aniline (1·9 g.) was melted at 185-190° and then copper powder (10 g.) was added. The mass was heated at 160-170° for 4 hours with occasional stirring. The dark mass was powdered and washed successively with dilute hydrochloric acid and sodium carbonate solution. It was then extracted with hot alcohol; the alcoholic solution yielded on dilution with water a brownish solid which was twice crystallised from alcohol (charcoal) in colourless rectangular plates, m.p. 205°, yield 3·5 g. (Found · N, 11·91. $C_{22}H_{17}O_2N_3$ requires N, 11·83 per cent). It is insoluble in cold dilute alkali, but dissolves in cold concentrated hydrochloric acid, being precipitated unchanged on standing or on dilution with water. It remains unchanged by the action of acetic anhydride and fused sodium acetate

The above compound was boiled with strong hydrochloric acid for about 2 hours and diluted with water. The clear solution was concentrated to a small bulk, when a crystalline mass was obtained which was filtered and triturated with cold water. The insoluble portion, on crystallisation from hot water, was proved to be hippuric acid. The aqueous solution on concentration yielded the hydrochloride (m.p 183-84°); the free base was obtained from the hydrochloride by treatment with aqueous sodium acetate solution and crystallised from benzene in colourless needles, m.p. 130°. Its identity with *o*-aminobenzanilide was confirmed by studying its properties and finally by analysis.

4-Keto-2-benzoylaminomethyl-3-p-tolyl-3:4-dihydroquinazoline (II, R = *p*-tolyl)—The method of preparation was the same as in the case of the previous compound. The compound crystallised from alcohol (charcoal) in colourless rectangular plates, m.p. 195-96°. (Found : N, 11·27. $C_{23}H_{19}O_2N_3$ requires N, 11·38 per cent). It is insoluble in cold dilute alkali, *4-Keto-2-benzoylaminomethyl-3-*m*-tolyl-3:4-dihydroquinazoline* (II, R = *m*-tolyl).—The method of preparation was the same as in the case of the previous compound (II, R = phenyl). The compound crystallised from alcohol (charcoal) in colourless rectangular plates, m.p. 177-78°; yield nearly 50%. (Found: N, 11·50. $C_{23}H_{19}O_2N_3$ requires N, 11·38 per cent). It is insoluble in alkali.

Condensation of the Compound (I) *with* o-*Phenylenediamine: Formation of 2-Benzoylaminomethyl-3:4-dihydroquinazoline-3:4-benziminazole* (IV). —An intimate mixture of the compound (I, 5·6 g.) and *o*-phenylenediamine (2·2 g.) was melted at 190° and then copper powder (10 g.) was added. The mass was heated at 170-180° for 4 hours. The dark mass was powdered and treated with cold dilute hydrochloric acid. The acid solution was filtered and treated with excess of sodium bicarbonate solution. The solid, thus obtained, was dried and extracted with absolute alcohol; the alcoholic solution, on dilution with water, gave a brownish crystalline precipitate which was twice crystallised from alcohol (charcoal) in colourless needles, m.p. 211-12°, yield 2·5 g. (Found: C, 74·78; H, 4·88; N, 16·12. $C_{22}H_{16}ON_4$ requires C, 75·0; H, 4·54; N, 15·91 per cent). It is insoluble in cold dilute alkali It does not contain any diazotisable amino group and does not form any acetyl derivative with acetic anhydride. It does not condense with phenyl *iso*cyanate, indicating thereby the absence of any free amino group

The above compound dissolves in dilute hydrochloric acid and the solution, on evaporation, yields the hydrochloride in the form of colourless plates, m.p. 225-31°. The hydrochloride was found contaminated with slight gummy matter, which, however, could not be removed by several crystallisations. When treated with aqueous sodium bicarbonate solution, it yields the original compound (IV). The compound (IV) has been found to remain stable when boiled with concentrated hydrochloric acid for about 45 minutes, the above hydrochloride being formed by this treatment.

Condensation of the Compound (I) *with* o-*Nitroaniline*.—Following the above method, the condensation was tried in presence of copper powder at 170-180° and at higher temperatures, but the condensation could not be effected.

My thanks are due to Prof. P. C Guha for his kind interest in this investigation. My thanks are due to the Lady Tata Memorial Trust for the award of a scholarship.

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STUDIES ON THE FORMATION OF DYES DERIVED FROM 8-OXYQUINOLINE ALDEHYDES AND FROM 2-OXYANTHRAQUINONE ALDEHYDE.

By Susil Kumar Ray.

Little investigations appear to have been made both on triphenylmethane as well as on pyronine dyes containing quinoline or anthraquinone nucleus. These dyes are of much interest on account of the presence of the condensed and heterocyclic ring systems. In the present paper some interesting pyronine and triphenylmethane dyes derived from 5- and 7-aldehydo-8-oxyquinoline and from 1-aldehydo-2-oxyanthraquinone have been described.

5-Aldehydo-8-oxyquinoline and 7-aldehydo-8-oxyquinoline were prepared by the action of chloroform on 8-oxyquinoline in presence of alkali, while the 1-aldehydo-2-oxyanthraquinone was prepared similarly from 2-oxy-anthraquinone (*cf.* Sen and Ray, *J Indian Chem. Soc* , 1932, **9**, 174). By the condensation of the quinoline aldehydes with dimethylaniline and also with resorcinol in presence of concentrated hydrochloric acid as the condensing agent, dyes of triphenylmethane type have been obtained, the leuco-bases on oxidation with lead peroxide in the usual way give the corresponding carbinols. The condensation with *o*-cresotinic acid has been effected in presence of concentrated sulphuric acid The leuco-base obtained, when oxidised with nitrosyl sulphate, dyes silk and wool a beautiful orange shade. The dimethylaniline compound dyes wool and silk, from dilute acetic acid bath, a deep blue shade, while the resorcin compound produces a magnificent golden yellow shade. Pyronine dyes have been obtained by condensing the aldehydes with diethyl *m*-aminophenol and with resorcinol in presence of concentrated sulphuric acid. The diethyl-*m*-amino compound produces a reddish violet shade on wool and silk, while the compound with resorcinol dyes silk and wool a delightful reddish orange shade. It is of interest to note that when the pyrone ring is not closed (*i.e.*, as in the condensation between the aldehyde and resorcinol in presence of concentrated hydrochloric acid) silk and wool are dyed a golden yellow shade, while by closing the pyrone ring the colour is deepened to reddish orange.

1-Aldehydo-2-oxyanthraquinone has also been successfully condensed with (*i*) dimethylaniline, using hydrochloric acid as the condensing agent ; (*ii*) *o*-cresotinic acid and (*iii*) diethyl *m*-aminophenol in presence of concentrated sulphuric acid. It has been noticed that the C=O groups in the anthraquinone ring do not react in these condensations. The compound with dimethylaniline, on oxidation with lead peroxide, dyes silk a delightful bluish violet shade while a greenish blue shade is produced on wool. The diethyl-*m*-amino compound produces a reddish violet shade on wool and silk, while the compound with *o*-cresotinic acid, on oxidation with nitrosyl sulphate, dyes silk a light yellow and wool a deep yellow shade which changes to reddish shade by after-chroming.

As the methods of preparation and properties of the corresponding condensation products of 5- and 7-aldehydo-8-oxyquinolines are identical, only those of 7-aldehydo-8-oxyquinoline have been given in Table I.

EXPERIMENTAL.

TABLE I.

Dyes derived from 7-aldehydo-8-oxyquinoline.

Condensation with	Procedure and analysis.
Dimethylaniline.	Aldehyde (2 g.) and dimethylaniline (5 c.c.) were heated on a boiling water-bath for 30 hours with frequent addition of concentrated hydrochloric acid (5 c.c. in all); the solution was made alkaline, distilled in steam, filtered and acidified with HCl and reprecipitated with ammonia. It crystallised from chloroform as a bluish green powder, m.p. 177°, yield 70%. It is insoluble in water, alcohol and ether; easily soluble in chloroform The carbinol base dyes silk and wool a deep blue shade from dilute acetic acid bath (Found: N, 10·76. $C_{26}H_{27}ON_3$ requires N, 10·58 per cent).
Resorcinol.	Aldehyde (2 g.) and resorcinol (4 g.) were heated with concentrated HCl (10 c.c.) for 20 hours and treated in the same manner as above The compound, precipitated with ammonia is a faint yellow powder. It crystallised from alcohol in black shining plates, m.p. 148°, yield theoretical. It is insoluble in water, ether and chloroform; sparingly soluble in acetone and acetic acid; moderately soluble in hot alcohol. The carbinol base dyes wool and silk a greenish yellow shade. (Found: N, 3·87. $C_{22}H_{17}O_5N$ requires N, 3·73 per cent).
o-Cresotinic acid.	Aldehyde (2 g.) and *o*-cresotinic acid (2·5 g.) when stirred with concentrated sulphuric acid (12 g.) for 5 hours at room temp. gave a liquid product which was oxidised with nitrosyl sulphate in the usual way; the mixture poured into water and filtered. It is soluble in sodium bicarbonate and insoluble in most organic solvents. It is a yellowish powder, m.p. above 250°. It dyes wool and silk an orange shade.
Diethyl *m*-aminophenol.	Aldehyde (2 g.) and diethyl-*m*-aminophenol (5 g.) when heated with concentrated sulphuric acid (20 c.c.) in an oil-bath for 4 or 5 hours at 120-130° gave a product which was treated with water and filtered. The filtrate was basified with ammonia when a reddish violet powder was obtained. It crystallised from alcohol as a violet powder softening at 80°, yield 90%. It is easily soluble in alcohol (pink solution with slightly violet fluorscence); sparingly soluble in ether; insoluble in petroleum ether and chloroform. It dyes silk and wool a reddish violet shade. (Found: N, 9·3. $C_{30}H_{35}O_3N$ requires N, 8·7 per cent).

Condensation with	Procedure and analysis.
Resorcinol in presence of H_2SO_4.	A mixture of aldehyde (2 g.) and resorcinol (4 g.) when heated with concentrated H_2SO_4 in the usual manner yielded a reddish powder which crystallised from alcohol in black shining plates melting at 86-87°, yield theoretical. It is easily soluble in alcohol (orange-red solution with yellowish green fluorescence); soluble in alkali with green fluorescence It dyes wool and silk an orange-red shade. (Found : N, 4·01 $C_{23}H_{13}O_5N$ requires N, 3·7 per cent).

TABLE II.

Dyes derived from 1-aldehydo-2-oxyanthraquinone.

Dimethylaniline.	A mixture of aldehyde (2 g.) and dimethylaniline (3 c.c.) when heated on a boiling water-bath with concentrated HCl (5 c.c.) and treated in the usual way gave a product which crystallised from alcohol as bluish green microcrystalline powder, m. p. 78°, yield 70%. It is insoluble in water and petroleum ether; sparingly soluble in alcohol and ether; moderately soluble in chloroform. The carbinol base dyes silk and wool a bluish violet shade. (Found · N, 5·8%. $C_{31}H_{28}O_3N_2$ requires N, 5·8 per cent).
Diethyl-*m*-aminophenol.	Aldehyde (2 g) and diethyl *m*-aminophenol (3 g.) when heated with concentrated H_2SO_4 and treated subsequently as in the preceding compound gave a violet product which crystallised from dilute alcohol as a violet powder, m.p. 135°, yield 90% It is insoluble in water, easily soluble in alcohol (pink), ether (yellow soln.), chloroform and acetone and insoluble in petroleum ether. It dyes wool and silk a reddish violet shade. (Found N, 5·21. $C_{35}H_{34}O_5N_2$ requires N, 4·99 per cent).
o Cresotinic acid	The condensation was effected in the same manner as with 7-aldehydo-8-oxyquinoline The product was a yellowish powder insoluble in most organic solvents hence it could not be purified for analysis It dyes wool and silk a yellowish shade which becomes reddish on after-chroming.

The author takes this opportunity of expressing his indebtedness to late Prof. R. N. Sen for the kind interest he took in the work.

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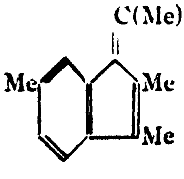
TERPENE COMPOUNDS. PART I SYNTHETIC STUDY ON THE STRUCTURE OF AZULENE

By Nripendra Nath Chatterjee.

Two structural formulæ (I) and (II) have been suggested for the blue pigment which is associated with the high boiling fractions of certain volatile oils (Kremers, *J. Amer. Chem Soc.*, 1923, **45** 717,; Ruzicka and Rudolf, *Helv. Chim. Acta*, 1926, **9**, 118; Ruzicka and van Veen, *Annalen*, **476**, 70; Ruzicka and Haagen-Smit, *Helv. Chim. Acta*, 1931, **14**, 1929, 1104; Birrel, *J. Amer. Chem. Soc.*, 1934, **56**, 1248; 1935, **57**, 883; Melville, *ibid.*, 1933, **55**, 3288; Birrel, *ibid.*, 1935, **57**, 893). The structure (I) was advocated by Kremers (*loc. cit.*) and (II) by Ruzicka and Haagen-Smit (*loc. cit.*) as explaining many known facts concerning the substance.

Preliminary experiments which have been carried out in this direction with the object of synthesising (I) are now described.

Ethyl Δ^1-tetrahydrobenzoate is condensed with ethyl sodio-cyanoacetate, and the resulting sodio derivative is allowed to react with ethyl bromoacetate, when ethyl 1-carbethoxy*cyclo*hexane-2-α-cyanosuccinate (III) is obtained (*cf.* Bardhan and Chatterjee, *J. Chem. Soc.*, 1935, 479). This on hydrolysis gives 1-carboxy*cyclo*hexane-2-succinic acid (IV). The ethyl ester of the above acid is cyclised with granulated sodium to yield ethyl (0.3:4-*bicyclo*)-nonan-2-one-3:4-dicarboxylate (V). This on hydrolysis gives the required (0.3:4-*bicyclo*)-nonan-2-one-4-carboxylic acid (VI). The corresponding keto-ester is treated with methyl magnesium iodide to yield a neutral product (VII), which on dehydrogenation with selenium probably furnishes (VIII).



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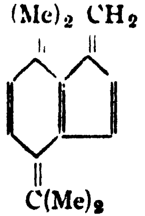

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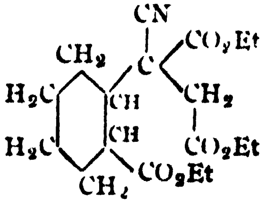

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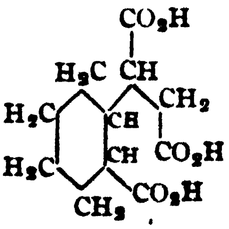

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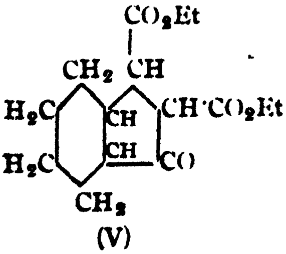

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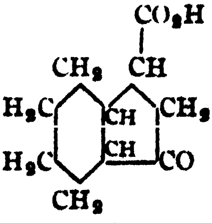

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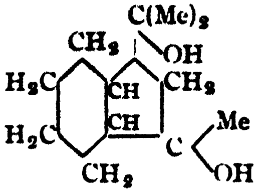

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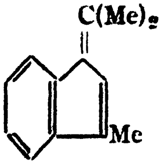

(VIII)

Experiments on simiiar lines are in progress with *p*-methyl*cyclo*hexanone for the synthesis of the compound (I) given above.

EXPERIMENTAL.

Ethyl Δ^1-tetrahydrobenzoate was prepared according to the following method in good yield. *cyclo*Hexanone (100 g.) was shaken with a solution of sodium bisulphite (200 g.) in water (250 c.c) and the mixture was cooled in ice and gradually treated with a solution of potassium cyanide (80 g.) in water (150 c.c.). After 2 hours the cyanohydrin was extracted with ether, washed with water and then with a saturated solution of sodium chloride, dried (anhydrous sodium sulphate), and the solvent removed with the addition of 2 drops of concentrated sulphuric acid. The crude cyanohydrin was refluxed with 5-6 volumes of concentrated hydrochloric acid (*d* 1·19) for 7 hours on the steam-bath and the hydroxy-acid extracted with ether, yield 105 g. The hydroxy-acid (50 g.) was treated with phosphorus pentachloride (140 g.) and heated on the water-bath for about 12 hours. The reaction product was cooled, poured into ice-cold absolute alcohol (200 c.c.) and left overnight. It was then diluted with water and the chloro-ester (100 g) was refluxed with alcoholic potash (100 g. in 300 c.c. of alcohol) for about 2 hours on the water-bath. After dilution, alcohol was removed on the water-bath as completely as possible, the brown solution cooled, filtered and acidified with hydrochloric acid, and the product collected in ether, dried and ether removed; yield 35 g. Ethyl Δ^1-tetrahydrobenzoate was prepared by a refluxing a mixture of the acid (161 g.), absolute alcohol (400 c.c.) and concentrated H_2SO_4 (61 c.c.) for 6 hours, b.p. 96°/10 mm., yield 165 g.

*Ethyl 1-Carbethoxy*cyclo*hexane-2-α-cyanosuccinate* (III).—A solution of sodium (4·6 g.) in absolute alcohol (75 c.c.) was cooled in ice and gradually mixed with ethyl cyanoacetate (22·6 g.). After half an hour ethyl Δ^1-tetrahydrobenzoate (33·6 g.) was added, and the mixture refluxed on the steam-bath for 24 hours. The brownish crystalline mass, consisting of the sodio derivative of the condensation product, was cooled in ice and treated with ethyl bromoacetate (33·6 g.), the mixture being finally heated for 6 hours. After cooling, the product was poured into water, and the oil extracted with ether, washed, dried, and fractionated under reduced pressure. Ethyl 1-carbethoxy*cyclo*hexane-2-α-cyanosuccinate had b. p. 204-206°/4 mm., yield 45 g. (Found: C, 61·1; H, 7·6. $C_{18}H_{27}O_6N$ requires C, 61·1; H, 7·6 per cent).

Ethyl 1-*Carboxy*cyclo*hexane*-2-*succinate* (IV).—A solution of the above cyano-ester (III, 40 g.) in concentrated sulphuric acid (45 c.c.) was diluted with water (320 c.c.) and refluxed for 50 hours on a sand-bath. Practically the whole of the acid went into solution. After cooling, the mixture was diluted with water and extracted with ether. The gummy acid (30 g.) obtained was converted by the alcohol vapour method into ethyl 1-carboxy*cyclo*hexane-2-succinate, a colourless limpid oil, b. p. 177°-185°/7 mm., yield 25 g. (in a typical experiment 65 g. of acid, 120 c.c. of absolute alcohol, 12 c.c. of concentrated sulphuric acid were treated and 3 litres of alcohol vapourised for 4 hours). (Found: C, 62·5; H, 8·5. $C_{17}H_{28}O_6$ requires C, 62·1; H, 8·53 per cent).

Ethyl (0:3:4-bicyclo)-*Nonan*-2-*one*-3:4-*dicarboxylate* (V).— The above ester (IV, 8 g.) was heated with granulated sodium (1·2 g.) and benzene (25 c.c.) until the whole of the sodium disappeared (2 hours). After cooling, the product was treated with cold dilute sulphuric acid and the benzene layer was washed with aqueous sodium carbonate and with water, dried, and evaporated. The residue gave a violet colouration with ferric chloride. The ester was obtained as a colourless oil, b.p. 188°/8mm., yield 4·5 g. (Found: C, 63·4; H, 8·0. $C_{15}H_{22}O_5$ requires C, 63·8; H, 7·8 per cent).

(0:3:4-bicyclo)-*Nonan*-2-*one*-4-*carboxylic Acid* (VI).—The product (28 g.) was refluxed with excess of dilute sulphuric acid (20%) for 12 hours; the cooled solution was saturated with ammonium sulphate and repeatedly extracted with ether and the extract washed with water. On removing ether the keto-acid crystallises, m.p. 136°, yield 18 g. (Found: C, 65·8; H, 7·6. $C_{10}H_{14}O_3$ requires C, 65·9; H, 7·6 per cent).

The *semicarbazone* crystallised from alcohol, m p. 220°. (Found: N, 17·2. $C_{11}H_{17}O_3N_3$ requires N, 17·5 per cent).

The *ethyl ester* was prepared by refluxing a solution of the keto-acid (VI, 18 g.) in absolute alcohol (68 c c.), saturated at 0° with hydrochloric acid gas and working up the product in the usual manner, b.p. 143-44°/8mm. (Found: C, 68·5; H, 8·4. $C_{12}H_{18}O_3$ requires C, 68·5; H, 8·5 per cent).

The *semicarbazone* crystallised from alcohol, m.p. 159°. (Found: N, 15·6. $C_{13}H_{21}O_3N_3$ requires N, 15·7 per cent).

Ethyl 3-*Methyl*- (0:3:4- bicyclo)-*nonan*- 2-*one*-3:4-*dicarboxylate*.—The ester of the compound (IV) (8 g.) was cyclised with sodium (1·2 g.) in benzene. The product was cooled in ice and gradually treated with excess of methyl iodide and the whole warmed until neutral. The mixture was treated with cold water and the benzene layer separated, dried and distilled, ethyl 3-methyl-(0:3:4-*bicyclo*)-nonan-2-one-3:4-dicarboxylate being obtained as a colourless oil, b.p. 174°/7mm., yield 4 g. It did not give a colouration with ferric chloride. (Found: C, 64·9 ; H, 8·1. $C_{16}H_{24}O_5$ requires C, 64·8 ; H, 8·1 per cent).

Action of Methyl Magnesium Iodide on Ethyl (0:3:4-*bicyclo*)-*nonan*-2-*one*-4-*carboxylate*: *Formation of Compound* (VII).—The ester (10 g.), diluted with dry ether (10 c.c.), was slowly added to a solution of methyl magnesium iodide (prepared from 3·6 g. of magnesium in 100 c c. of dry ether and 11 c.c. of methyl iodide) cooled in ice-water. After standing for 12 hours at the ordinary temperature the product was decomposed with ice and dilute hydrochloric acid. The solution was extracted ten times with ether and the extract was washed with water, dried and evaporated. The brown residue was boiled with a solution of potassium hydroxide (10 g.) in water (10 c.c.) and alcohol (90 c.c.) for 1 hour; the alcohol was removed as completely as possible and the residue diluted with water and repeatedly extracted with ether, yield 4 g. The neutral product thus obtained exhibits bluish fluorescence in ethereal solution, b.p. 154°/4mm. (Found: C, 74·4; H, 10·7. $C_{13}H_{24}O_2$ requires C, 73·6; H, 11·3 per cent).

1-iso*Propylidene*-3-*methylindene* (VIII).—The neutral product (VII) was heated with selenium at 300-320° for about 29 hours. The product (probably a mixture) was extracted with ether and after removing the solvent fractionated and a small quantity of a substance at 145-48°/11 mm. was collected and crystallised from methyl alcohol, m.p. 49°. (Found: C, 90·5; H, 8·0. Calc. for $C_{13}H_{14}$: C, 91·7 ; H, 8·2 per cent).

My sincere thanks are due to Professor P. C. Mitter for encouragement and advice during the course of this work.

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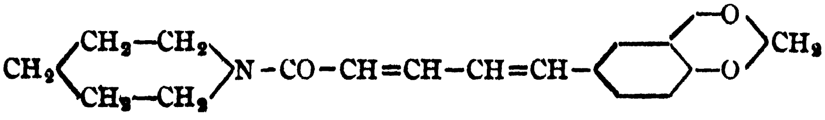
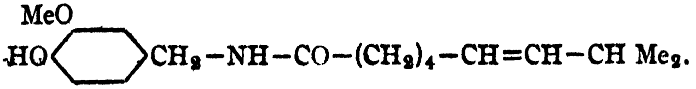
SYNTHESIS OF SUBSTANCES RELATED TO CAPSAICIN.

By P. C. Mitter and Sudhir Chandra Ray.

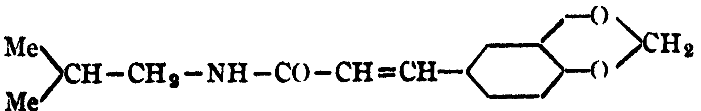
The naturally occurring pungent principles like piperine, capsaicin, fagaramide, spilanthol, pellitorine etc., are found to possess in common the acyl amide -N-CO- linking, the amine being either primary or secondary. It may be purely aliphatic, *viz.*, *iso*butylamine in fagaramide or fat-aromatic like vanillylamine (in capsaicin) or heterocyclic like piperidine (in piperine). The acid is either aliphatic or fat-aromatic and in all the naturally occurring pungent principles, hitherto investigated, contains at least one ethylenic linkage.



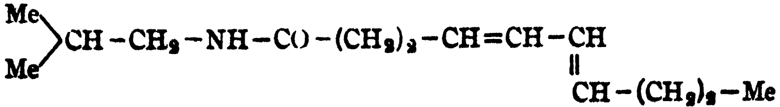
(Piperine)



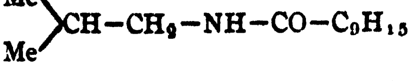
(Capsaicin)



(Fagaramide)



(Spilanthol)



(Pellitorine, position of double bonds unknown.)

A number of synthetic pungent principles have also been prepared and studied. Thus Scholtz (*Ber.*, 1895, **28**, 1196) has found that the homologues of piperine and further the piperidide of methylene caffeic acid have got the piperine taste.

Nelson (*J. Amer. Chem. Soc.*, 1919, **41**, 1115; 1920, **42**, 597; Nelson and Dawson, 1923, **45**, 2179) after establishing the constitution of capsaicin prepared and studied the vanillylamides of acetic, propionic, butyric, *iso*butyric, *n*-hexoic, *n*-heptoic, *n*-octoic, *n*-nonoic, *n*-decoic, crotonic and Δ^{10}-undecylenic acids. He found that the pungency as determined by Pearson's method (*Pharm. J.*, 1919, **103**, 78) increased until it reached a maximum in *n*-nonovanillylamide and then decreased as the molecular weight increased.

Ott and Zimmerman (*Annalen*, 1921, **425**, 314) found that the vanillylamides of unsaturated acids, especially oleovanillylamide, were very pungent while stearovanillylamide was tasteless. So they concluded that the pungency was associated with unsaturation in the acyl group. They also prepared the benzylamide as well as the methoxy- and hydroxybenzylamide of undecylenic acid and found that while the benzylamide and methoxybenzylamide were tasteless, 2-hydroxy- and 4-hydroxybenzylamides were pungent.

Nelson (*loc. cit.*) as well as Lapworth and Royle (*J. Chem. Soc.*, 1919, **115**, 1109) prepared the methyl ether of capsaicin and found that it was much less pungent than capsaicin. Nelson and Dawson (*loc cit.*) had shown that capsaicin and hydrogenated capsaicin were equally pungent At least in this case, therefore, unsaturation has no influence on pungency.

Jones and Pyman (*J Chem. Soc.*, 1925, **127**, 2588) using mainly Nelson's method (*J Amer Chem. Soc.*, 1919, **41**, 2121) prepared the vanillylamides of various acids including aliphatic normal and branched chain acids, benzoic acid, saturated ω-phenyl-fatty acids and halogenoacetic acids Besides they prepared substituted benzylamides of *n*-nonoic and $\Delta^{\prime\prime}$-undecylenic acids They observed that while the vanillylamides of saturated phenyl fatty acids were pungent, benzovanillylamide was only faintly so Cinnamovanillylamide was practically tasteless, while its dihydro derivative was pungent. Some of the aliphatic acid compounds were pungent, while others were practically devoid of pungency. Of the substituted benzylamides of the acids mentioned above, those containing phenolic hydroxyl groups were pungent, while methoxy and methylenedioxy compounds were tasteless.

We have synthesised a number of acylated *iso*butylamines to see if the pungency depends in any way on the lengths of the carbon chains, on the position of the double bonds, if any, and also on the character of the acids, aliphatic or aromatic or fat aromatic.

Our conclusions are as follows :—

(1) *iso*Butylamides of Δ^{2}-heptenoic and Δ^{3}-nonenoic acids are equally strongly pungent. *n*-Heptoi*so*butylamide is next in order of pungency, which therefore decreases to some extent with saturation,

(2) Benzo*iso*butylamide is also very pungent but aniso*iso*butylamide is practically devoid of pungency.

(3) The *iso*butylamide of *n*-hexoic, Δ^2-hexenoic, *n*-octoic, Δ^2-octenoic and Δ^3-decylenic acids are equally pungent but the pungency is of a lower order.

(4) The *iso*butylamide of Δ^ω-undecylenic acid is very feebly pungent hence the pungency decreases when the acyl chain is long and the unsaturated linking remote from the -N-CO- group.

EXPERIMENTAL.

*n-Hexo*iso*butylamide.*—Caproic acid (1 mol., 12 g.) and thionyl chloride (8 c.c.) were taken in a flask (250 c.c.) fitted with a condenser, dropping funnel and $CaCl_2$ guard tubes. It was warmed on the water-bath and shaken from time to time until the evolution of gases ceased. The flask was cooled in ice and nearly 100 c c. of sodium-dried benzene were added. *iso*Butylamine (2 mol., 15 g.) was added drop by drop from the tap funnel, the flask being vigorously shaken after each addition. It was allowed to stand overnight and then warmed on the water-bath for about ½ hour. After cooling, water was added and then the flask was warmed on the water-bath for about ½ hour. Finally the oily layer was extracted with ether and washed successively with water, very dilute hydrochloric acid, water, soda solution and finally again with water. After drying over anhydrous calcium chloride, the ether-benzene mixture was distilled off from a water-bath. The residue was kept in a vacuum desiccator for a day and then distilled at 136°/9 mm. (Found : N, 8·22. $C_{10}H_{21}ON$ requires N, 8·19 per cent).

*Δ^2-Hexeno*iso*butylamide.*—Hexenoic acid was prepared by condensing *n*-butylaldehyde with malonic acid in presence of piperidine and purified according to the method of Fittig (*Ber.*, 1894, **27**, 2667). The acyl chloride prepared in the usual manner was condensed with *iso*butylamine without a solvent as it was found that when anhydrous ether or benzene was used the yield of the amide was very poor. It boiled at 138°/4mm. (Found · N, 8 27. $C_{10}H_{19}ON$ requires N, 8·28 per cent).

n-*Hepto*iso*butylamide.*—*n*-Heptoic acid was prepared by oxidising oenanthol according to the method of Grimshaw and Schorlemmer (*Annalen*, 1873, **170**, 141). The chloride of the acid was condensed with *iso*butylamine in presence of dry benzene. It boils at 130°/7 mm. (Found : N, 7·93. $C_{11}H_{23}ON$ requires N, 7·57 per cent).

*Δ^2-Hepteno*iso*butylamide.*—Oenanthylic acid was converted into α-bromoenanthylic ester according to the method of Rupe, Ronus and Lotz (*Ber.*, 1902, **35**, 4268). The bromo-ester was converted into Δ^2-heptenoic ester

by the method of Crossly and LeSueur (*J. Chem. Soc.*, 1899, **75**, 166). The latter gave on hydrolysis heptenoic acid, b.p. 129-132°/20 mm. The amide was prepared in the usual manner, b.p. 140°/4mm. (Found : N, 7·49. $C_{11}H_{21}ON$ requires N, 7·65 per cent).

n-*Octoisobutylamide*.—The chloride of caprylic acid was condensed with *iso*butylamine in the usual manner, b.p. 155°/8mm. (Found : N, 7·32. $C_{12}H_{25}ON$ requires N, 7·03 per cent).

Δ^2-*Octenoisobutylamide*.—Caprylic acid was converted into α-bromocaprylic ester according to the method of Auwers and Bernhardi (*Ber.*, 1891, **24**, 2223) and the bromo-ester converted into Δ^2-octenoic acid according to Crossley and LeSueur (*loc. cit.*). The ester gave on hydrolysis Δ^2-octenoic acid, which was condensed with *iso*butylamine in the usual manner, b.p. 150°/4 mm. (Found : N, 7·22. $C_{12}H_{23}ON$ requires N, 7·11 per cent).

Δ^2-*Nonenoisobutylamide*.—Δ^2-Nonenoic acid was prepared according to the method of Harding and Weizmann (*J. Chem. Soc.*, 1910, **97**, 301) and purified by the hypoiodous acid method (Bougault, *Compt. rend.*, 1904, **139**, 864). The amide prepared in the usual manner boils at 170°/7 m.m. (Found : N, 6·90. $C_{13}H_{25}ON$ requires N, 6·63 per cent).

Δ^3-*Decylenoisobutylamide*.—Distillation of *n*-hexylparaconic acid, prepared according to the method of Fittig (*Annalen*, 1885, **227**, 90) yielded Δ^3-decylenic acid, the chloride of which was condensed with *iso*butylamine, b.p. 155°/4 mm. (Found : N, 6·06. $C_{14}H_{27}ON$ requires N, 6·22 per cent).

Δ^{ω}-*Undecylenoisobutylamide*.—Δ^{ω}-Undecylenic acid was prepared from castor oil according to the method of Jones and Pyman (*loc. cit.*). Δ^{ω}-Undecyleno*iso*butylamide boils at 175°/5mm. (Found: N, 5·89. $C_{15}H_{29}ON$ requires N, 5·86 per cent).

Benzoyl, anisoyl and cinnamoyl chlorides were condensed with *iso*butylamine in the usual manner. *Benzoisobutylamide*, melts at 55° (Found : N, 8·13. $C_{11}H_{15}ON$ requires N, 7·91 per cent). *Anisoisobutylamide* melts at 105-106° (Found : N, 6·93. $C_{12}H_{17}O_2N$ requires N, 6·76 per cent). *Cinnamoisobutylamide* melts at 114° (Found : N, 6.98. $C_{13}H_{17}ON$ requires N, 6·90 per cent).

The pungency was determined by Pearson's method (*loc. cit.*) in each case. Alcoholic solutions (1%) of the compounds were prepared. From each solution, a known volume was pipetted out and diluted with an equal volume of alcohol. A few drops were placed on the tongue and the result noted. The dilution was continued until a few drops when put on the tongue did not produce any perceptible effect.

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ON THE PHOTOBROMINATION OF ACETYLENE DICHLORIDE IN THE GASEOUS PHASE.

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M. L. Narasimha Murthi.

It is well known that the unimolecular velocity constant of decomposition of nitrogen pentoxide in the gaseous phase and in various solvents is the same at the same temperature. This relation also holds good in the case of another unimolecular reaction—racemisation of pinene. But the number of cases, in which a comparative study of reactions in the gas phase and in solutions of some inert solvents has been made, is very small. In a previous paper (*Z. physikal. Chem.*, 1936, **B**, **32**, 145) Ghosh and Bhattacharyya have studied the photobromination of acetylene dichloride in solution of carbon tetrachloride in 406, 436 and 546$\mu\mu$ and in the gaseous phase in 436$\mu\mu$ only. They have shown that the kinetics of the photobromination are the same in the gaseous phase as well as in solution of carbon tetrachloride, only the reaction in the gas phase has been found to be about 30 times faster than that in solution of carbon tetrachloride.

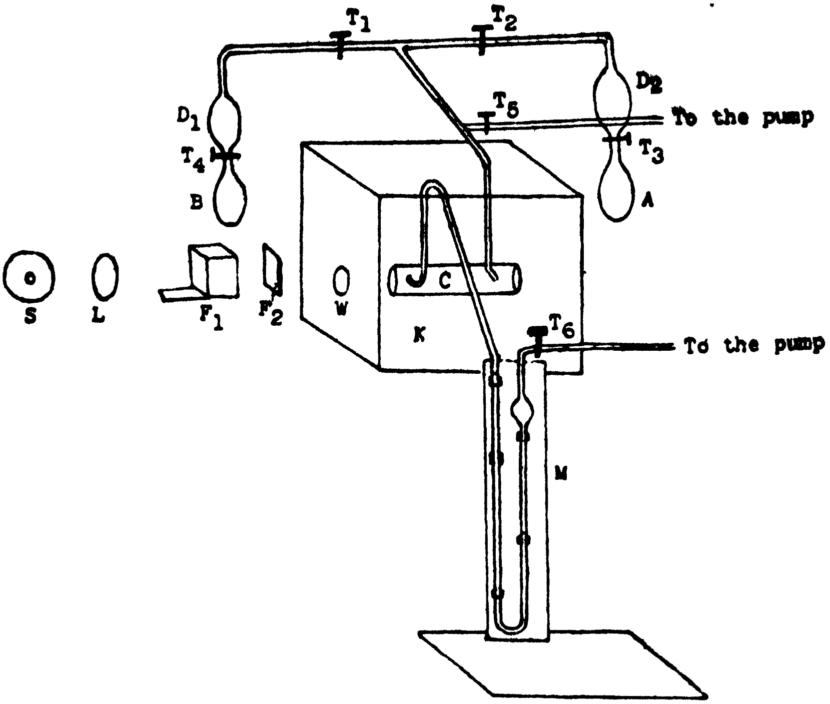
The object of the present investigation was to make a thorough comparative study of the same reaction in 546$\mu\mu$.

EXPERIMENTAL.

In these experiments the reaction was followed by measuring the pressure change. The green light (546$\mu\mu$) was isolated from a mercury point-o-lite lamp by means of suitable " Zeiss monochromat " filters. The apparatus is shown in Fig. 1. The reaction vessel C is a quartz cylindrical cell with plane parallel faces fused on (11 cm. in length and 2 cm. in diameter) and provided with two side-tubes bent at right angles and with ends grounded. One of the side-tubes is connected with the reservoirs of bromine and acetylene dichloride through vacuum stop-cocks T_1, T_2, T_3 and T_4 and bulbs D_1 and D_2 by fine capillary tubings. Another connection is made to the pump through a stop-cock T_5. The other side-tube is connected to the pressure gauge.

The pressure gauge consists of a sulphuric acid manometer with a bulb blown in one end, which is connected to the pump through a stop-cock T_6. Vacuum grease containing rubber was saturated with bromine vapour for about a month before use.

FIG. I



[A—reservoir of bromine , B—reservoir of acetylene dichloride, C—reaction cell; F_1—$CuSO_4$ filter, F_2—Zeiss monochromatic filter, K—thermostat, L—convex lens, M—manometer, S—point-o-lite lamp, T_1-T_6—stop-cocks]

The reaction vessel is contained in a thermostat K provided with a quartz window W through which light falls on the reaction cell. The temperature of the bath was kept constant to within 0·1°.

The last trace of air was removed from the apparatus by repeated washing with the vapour of bromine and acetylene dichloride which do not react in the dark.

Preliminary experiments showed that on an unclean surface there was sometimes no reaction and where there was a reaction it proceeded irregularly. For this, the reaction vessel was carefully washed after each experiment with chromic acid, caustic soda solution and hydrochloric acid and subsequently with water, ether and pure carbon tetrachloride, and then dried by sucking clear air through this by means of an efficient pump.

Merck's extra pure " Reagent " bromine and Kahlbaum's acetylene dichloride were used throughout the investigation.

The intensity of incident radiation was measured by means of a Moll thermopile and a Moll galvanometer, calibrated against a standard lamp tested by the " Bureau of Standards". The intensity of absorbed radiation was calculated by knowing the intensity of the incident radiation from the existing data on the extinction coefficient of bromine in the gaseous state made by Gray and Style (*Proc. Roy. Soc.*, 1930, **A126**, 603). These authors found that the extinction coefficient of bromine vapour, calculated with the gram mols per litre as the unit concentration and using logarithm to the base 10, was 29·6 for 546$\mu\mu$.

The Velocity Constant of the Reaction.

The constants in these experiments are calculated according to the simple unimolecular equation,

$$K=\frac{2\cdot3}{t}\log_{10}\frac{p_0}{p_0-x}$$

where p_0 denotes the initial partial pressure of bromine and p_0-x, the pressure of bromine after time t seconds.

All the experiments were done with the partial pressures of bromine less than its saturated vapour pressure at the same temperature, saturated vapour pressure of bromine being 26·45 cm. of Hg at 30° (Ramsay and Young, *J. Chem. Soc.*, 1886, **49**, 453).

It was always found that the values of K remained constant for sometime and then began to diminish slightly with time. This is probably due to the diminution of the concentration of the absorbing bromine.

Effect of Varying the Concentration of Bromine on the Velocity of Reaction.

TABLE I.

$\lambda=546\mu\mu$. Temperature $=30°$. I_0 = Intensity of incident radiation per sq. cm per sec. = 1488·5 ergs. P = Total gas pressure in cm. of H_2SO_4. $p(\text{Br}_2)$ = Partial pressure of bromine in cm. of H_2SO_4. t = Time in seconds. $p_0(\text{Br}_2)$ and $p_0(\text{A})$ denote respectively the initial partial pressures of bromine and acetylene dichloride in cms. of H_2SO_4.

	A. $p_0(\text{Br}_2)$ = 15·75 cm. of H_2SO_4; $p_0(\text{A})$ = 40 cm. of ,,			B. $p_0(\text{Br}_2)$ = 12·4 cm. of H_2SO_4, $p_0(\text{A})$ = 41·0 cm. of ,,		
t.	P.	$p(\text{Br}_2)$.	$K_6 \times 10^5$.	P.	$p(\text{Br}_2)$.	$K_6 \times 10^5$.
0 sec	55·75	15·75	...	53·4	12·40	...
180	51·75	13·75	75·4	50·5	10·95	69·9
360	48·25	12·0	74·5	47·9	9·65	69·6
540	45·25	10·5	74·4	45·6	8·50	69·8
720	42·65	9·2	74·1	43·6	7·50	69·7
900	40·30	8·025	74·4	41·9	6·65	69·1
1080	38·31	7·03	74·0	40·5	5·95	67·9
1260	36·71	6·23	73·2	39·3	5·35	66·6
1440	35·31	5·53	72·4			

$K_6 \times 10^5$ (mean) = 69·3.

$K_6 \times 10^5$ (mean) = 74·3

Similar readings were taken with other initial partial pressures of bromine and the results are tabulated in the following table.

TABLE II.

$p_0(\text{A})$ of acetylene dichloride = 40 cm. of H_2SO_4. C_0 of acetylene dichloride = 0·0032M. $[\text{Br}_2]$ = Initial concentration of bromine. $p_0(\text{Br}_2)$ = Initial partial pressure of bromine. $p_{360}(\text{Br}_2)$ = Partial pressure of bromine after 360 secs. I_0 = Intensity of incident radiation in ergs per sq. cm. per sec. I_{abs} = Intensity of radiation absorbed in ergs per c.c. per sec. The significance of K_6 will be found from the Discussion.

$\lambda = 546 \mu\mu$. $I_0 = 1488·5$.

Temp	$[\text{Br}_2]$ Mol.	$p_0(\text{Br}_2)$.	$p_{360}(\text{Br}_2)$.	$K_6 \times 10^5$.	I_{abs}	$\frac{K_6 \times 10^7}{I_{abs}}$.
30°	0·000985	12·4	9·65	69·3	70·4	838·0
,,	0·00126	15·75	12·0	74·5	82·3	821·4
,,	0·0016	20·0	14·95	80·5	94·5	830·0
40°	0·00126	15·75	10·80	104·4	82·3	1151·0

Effect of Varying the Concentration of Acetylene Dichloride on the Velocity of Reaction.

TABLE III.

$\lambda = 546\mu\mu$. $I_0 = 1488{\cdot}5$ ergs/sq. cm./sec. Temp. = 30°.
$p_0(\mathrm{Br}_2) = 12{\cdot}7$ cm. of H_2SO_4. $p_0(\mathrm{A}) = 20$ cm. of H_2SO_4.

t.	P	$p(\mathrm{Br}_2)$.	$K_6 \times 10^5$.	$K_6 \times 10^5$(mean)
0 sec.	32·7	12·70	34·0	34·6
180	31·2	11·95	...	
360	29·6	11·15	36·1	
540	28·3	10·50	35·1	
720	27·3	10·00	33·1	
900	26·4	9·55	31·5	
1080	25·6	9·15	30·3	

Similar readings were taken with other initial partial pressures of acetylene dichloride, keeping constant the initial partial pressure of bromine and the results are tabulated below.

TABLE IV.

Temp. = 30°. $\lambda = 546\mu\mu$.

$[\mathrm{A}]_0$ = Initial concentration of acetylene dichloride. $p_0(\mathrm{Br}_2) = 12{\cdot}5$ cm. of H_2SO_4. $[\mathrm{Br}_2]_0 = 0{\cdot}000985M$.

$p_0(\mathrm{A})$	$[\mathrm{A}]_0$	$p_0(\mathrm{Br}_2)$	$p_{360}(\mathrm{Br}_2)$.	$K_6 \times 10^5$	I_0.	I_{abs}	$\dfrac{K_6 \times 10^7}{I^{\frac{1}{2}}_{\mathrm{abs}}}$.
20·0	0·0016M	12·7	11·15	36·1	1488·5	70·4	429·7
41·0	0·00326	12·4	9·65	69·6	,,	,,	821·4
60·0	0·0048	12·4	9·20	82·8	,,	,,	985·7
20·0	0·0016	12·4	11·24	27·2	744·3	35·2	462·7
40·0	0·0032	12·5	10·5	48·6	,,	,,	823·7

Quantum Efficiency of the Process.

The calculation of the quantum efficiency has not much theoretical significance in this reaction, because the velocity observed is really due to reaction chains started by the Br atoms which attain a definite value at the stationary state. However, a comparison of the number of bromine molecules transformed per quantum of light absorbed in this reaction with that of reaction in the solution of CCl_4 may yield interesting results.

At the beginning of the reaction we may take it that the reaction is represented by the equation

$$\Delta x = K_6[\mathrm{Br}_2]\Delta T.$$

The significance of this equation will be found from the Discussion.

Taking the case of $p_0(\mathrm{A}) = 40$ cm. of H_2SO_4

$p_0(\mathrm{Br}_2) = 12{\cdot}4$ cm. of H_2SO_4. $[\mathrm{Br}_2]_0 = 0{\cdot}000985$ g. Mols/litre. $K_6 = 69{\cdot}3 \times 10^{-5}$ and $\lambda = 546\mu\mu$,

We get $\dfrac{\Delta x}{\Delta t} = 6{\cdot}82 \times 10^{-10}$ Mols. per c.c per sec.

$\therefore \quad \dfrac{\Delta x}{\Delta t} = 6{\cdot}82 \times 6{\cdot}06 \times 10^{13} = 4{\cdot}13 \times 10^{14}$ Br_2 molecules per c.c. per sec.

Again, the no. of quanta absorbed by 1 c.c. of the reaction mixture

$$= \frac{I_{abs}}{h\nu} = \frac{70{\cdot}4}{3{\cdot}6 \times 10^{-12}} \times 19{\cdot}6 \times 20^{12} = 0{\cdot}196 \times 10^{14}.$$

Hence the quantum efficiency $(\gamma) = \dfrac{4{\cdot}13 \times 10^{14}}{0{\cdot}196 \times 10^{14}} = \underline{21{\cdot}1}.$

In Table V are given the quantum efficiency for different concentrations of bromine and acetylene dichloride at 30°.

TABLE V(*a*).

Temp. = 30°.

$[\mathrm{Br}_2]_0 \times 10^4$.	$[A_0] \times 10^4$	$\left(\dfrac{\Delta x}{\Delta t}\right) \times 10^{13}$.	$\left(\dfrac{I_{abs}}{h\nu}\right) \times 10^{13}$.	γ.
9·85	32·0	41·5	1·06	21·1
12·6	32·0	57·3	2·28	25·1
16·0	32·0	78·6	2·63	29·9
12·6	32·0	79·9	2·28	35·0

TABLE V(*b*).

$[Br]_0 \times 10^4$.	$[A]_0 \times 10^4$.	$\left(\frac{\Delta x}{\Delta t}\right) \times 10^{-13}$.	$\left(\frac{I_{abs}}{h\nu}\right) \times 10^{-13}$.	γ.
9·85	16·0	21·7	1·96	11·0
9·85	32·6	41·3	1·96	21·1
9·85	48·0	49·7	1·96	25·3
9·85	16·0	16·3	0·98	16·7
9·85	32·0	29·2	0·98	29·8

The temperature coefficient is high.

Comparison of the Reaction Velocity in the Gas Phase with that in Solution of Carbon Tetrachloride.

The kinetics of the photobromination of acetylene dichloride in solution of CCl_4 have been studied in 546$\mu\mu$, 436$\mu\mu$ and previously in the gas phase in 436$\mu\mu$ by Ghosh and Bhattacharyya (*loc. cit.*). They have shown that the values of velocity constant in the gas phase become comparable with those in the CCl_4 solution only when $\frac{K_5 A}{K_4 + K_5 [A]}$ becomes almost unity (*vide* the Discussion).

This happens when $[A] > 0·0045M$. The comparable results are tabulated in Table VI.

TABLE VI.

	λ.	Temp.	Phase.	$[A_0]$.	$\frac{K_6 \times 10^7}{I^{\frac{1}{2}}_{abs}}$.	Ratio $\frac{\text{gas}}{CCl_4 \text{ soln.}}$
(*a*)	436 $\mu\mu$	30°	Gas	0·0052	1322·0	32
	,,	,,	CCl_4	0·0045	41·3	
(*b*)	546 $\mu\mu$	30°	Gas	0·0048	985·7	47
	,,	,,	CCl_4	0·0054	21·0	

From the above table it will be seen that in the case of 436$\mu\mu$, the ratio $\frac{K_6/I^{\frac{1}{2}}_{abs}\ (\text{gas})}{K_6/I^{\frac{1}{2}}_{abs}\ (CCl_4)}$ is about 32, whereas in 546$\mu\mu$ this ratio becomes about 47. This divergence is due to the fact that in CCl_4 solution, the velocity constant in 436$\mu\mu$ is about 2 times greater than that in 546$\mu\mu$, whereas in the gaseous state the velocity constant in 436$\mu\mu$ is only 1·4 times greater than that in 546$\mu\mu$.

DISCUSSION.

The reaction has the following characteristics :—

(1) The reaction is unimolecular with respect to bromine (Table I).

(2) The velocity constant falls slowly with time (Table I).

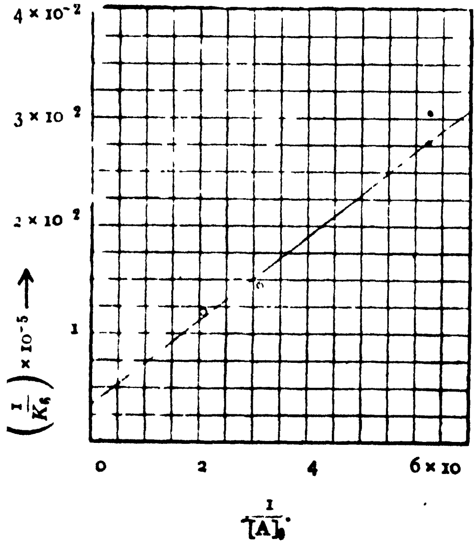
(3) The velocity constant is directly proportional to the square root of absorbed energy (Table III).

(4) The velocity constant diminishes with diminishing concentration of bromine and in fact $\left(\frac{K_6}{I^{\frac{1}{2}}_{abs}}\right)$ remains practically constant for all concentrations of bromine (Table II).

(5) The velocity constant increases about 1·4 times for 10° rise in temperature which is also the case in solution of CCl_4 (Table II).

(6) The inverse of K plotted against the inverse of the initial concentration of acetylene dichloride gives a straight line (Fig. 2).

FIG. 2.



The experimental data recorded above can be explained by the following mechanism of reaction :—

$$\mathrm{Br_2} + h\nu \rightarrow \mathrm{2Br} \quad \ldots \quad \ldots \quad (i)$$

$$\mathrm{Br} + \mathrm{Br} \rightarrow \mathrm{Br_2} \quad \ldots \quad \ldots \quad (ii)$$

$$\mathrm{Br} + \mathrm{Br_2} \rightarrow \mathrm{Br_3} \quad \ldots \quad \ldots \quad (iii)$$

$$\mathrm{Br_3} \rightarrow \mathrm{Br} + \mathrm{Br_2} \quad \ldots \quad (iv)$$

$$\mathrm{Br_3} + \mathrm{A} \rightarrow \mathrm{ABr_2} + \mathrm{Br} \quad \ldots \quad (v)$$

where A represents the acetylene dichloride molecule. The above mechanism gives for

$$K_6 = \frac{1}{[\mathrm{Br_2}]} \cdot \frac{d[\mathrm{Br_2}]}{dt} = K_3 \sqrt{\frac{I_{\mathrm{abs}}}{Nh\nu . K_2}} \cdot \frac{K_5[\mathrm{A}]}{K_4 + K_5[\mathrm{A}]}$$

$$= K_3 \left(\frac{I_{\mathrm{abs}}}{E\, K_2}\right)^{\frac{1}{2}} \cdot \frac{K_5[\mathrm{A}]}{K_4 + K_5[\mathrm{A}]} \quad \ldots \quad \ldots \quad (a)$$

where $E = N.\ h.\nu.$

From (a) it follows that $\frac{1}{K_6}$ plotted against $\frac{1}{[\mathrm{A}]}$ must give a straight line which has been found to be true.

The equation (a) also agrees well with the experimental observation recorded in Table III that K_6 varies as the square root of the energy of radiation absorbed.

From Table VI it will be seen that under comparable conditions of experiment, the reaction proceeds about 47 times ($\lambda = 546 \mu\mu$) faster in the gas phase than in $\mathrm{CCl_4}$ solution.

The two intermediate association reactions

$$\mathrm{Br} + \mathrm{Br} \rightarrow \mathrm{Br_2} \quad \ldots \quad (ii)$$

$$\mathrm{Br} + \mathrm{Br_2} \rightarrow \mathrm{Br_3} \quad \ldots \quad (iii)$$

require generally for fruitful collisions, the presence of a third body to carry away the excess energy. In the gas phase for the same amount of absorbed energy per c.c., the concentration of bromine atoms will necessarily be much larger than in the case of CCl_4 solutions.

The effect of the increased concentration of bromine atom is, however, counteracted by the retardation of reaction (*iii*) due to absence of the third body. An exact balance, however, is not attained, and the net result is that the velocity constant in the gas phase is much greater than in CCl_4 solution.

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POTENTIOMETRIC STUDIES IN OXIDATION-REDUCTION REACTIONS. PART III. REDUCTION WITH SODIUM SULPHITE.

By Balwant Singh and Ijaz Ilahi Malik.

Sulphurous acid and sulphites are reducing agents. Dymond and Hughes (*J. Chem. Soc.*, 1897, **71**, 314) studied the reducing action of sulphite on acidified potassium permanganate solution. They found that the oxygen used was 90 to 95% of that required for the oxidation of sulphite to sulphate. They accounted for this deficiency as due to the formation of dithionic acid, the potassium salt of which was isolated and analysed. The reaction is represented by the equation :

$$17H_2SO_3 + 6KMnO_4 = 2K_2S_2O_6 + K_2SO_4 + 6MnSO_4 + 6H_2SO_4 + 11H_2O.$$

Alkaline solutions of sulphur dioxide were found by Gilles (*Ann. chim phys.*, 1858, **55**, 374), Fordos and Gellis (*J. Pharm. chim.*, 1859, *iii*, **36**, 113) and Buignet (*ibid.*, p. 122) to be almost completely oxidised to sulphate by permanganate; but in acidic solution about one-fifth is oxidised to dithionate.

Hendrixson (*J. Amer. Chem. Soc.*, 1925, **47**, 1319, 2156) studied the oxidation of sulphurous acid by dichromate, bromate and iodate in acid solution. The amounts of dichromate and bromate are less than those required by theory for the complete oxidation to sulphate. This discrepancy is regarded as due to the formation of some dithionic acid which resists further oxidation. On the other hand iodate oxidises the sulphite completely to sulphate. The reaction with iodate is represented by the equations :

$$\begin{aligned} IO'_3 + 3SO''_3 &= 3SO''_4 + I' \\ IO'_3 + 6H^+ + 5I' &= 3I_2 + 3H_2O \\ 3I_2 + 3SO''_3 + 3H_2O &= 3SO''_4 + 6H^+ + 6I'. \end{aligned}$$

The oxidation is, therefore, effected by free iodine as in other ordinary iodine oxidations.

Hendrixson (*loc. cit.*) has further shown that sulphite is quantitatively oxidised in acid solution by bromate, dichromate or permanganate on the addition of one-half equivalent of iodide to these oxidants. In the present investigation, sodium sulphite has been used as a reducing agent in acid solution in presence of an excess of potassium iodide to determine iodine, potassium dichromate, potassium ferricyanide, copper sulphate and hydrogen peroxide by the potentiometric method.

EXPERIMENTAL.

A known weight of sodium sulphite was dissolved in freshly boiled water and the solution kept under hydrogen in a vessel connected with a hydrogen generator and a burette. The strength of the sulphite solution was checked against standard iodine.

A bright platinum foil dipping into a liquid in a titration vessel constituted one-half element; the other was the saturated calomel electrode connected through an agar-agar—KCl bridge. The mixture in the titration vessel was thoroughly stirred and the E.M.F. of the cell was measured on a potentiometric scale after each addition of the titrant.

The estimation of iodine was carried out by directly titrating it against the standard solution of sodium sulphite. In the case of potassium dichromate, potassium ferricyanide and copper sulphate, a known amount of each was mixed with an excess of potassium iodide solution, acidified and the liberated iodine titrated against the standard sodium sulphite. The titrations were conducted in the presence of carbon dioxide to prevent the atmospheric oxidation of hydriodic acid formed in the reactions.

To titrate hydrogen peroxide it was first acidified and then mixed with potassium iodide solution. A few drops of ammonium molybdate were then added to catalyse the reaction.

A series of potentiometric titrations were performed with different amounts of each substance. One titration for each substance, as typical of that set, is recorded in the following tables.

TABLE I.

Titration of 25 c.c. of $N/20$ iodine (0·1586 g.) against sodium sulphite ($N/10·08$).

Sodium sulphite.	E.M.F. (volts).	*E/C* (m.volts/c.c.).	Sodium sulphite.	E.M.F. (volts).	*E/C* (m.volts/c.c.).
11·50 c.c.	0·208		12·60	0·079	
		16			140
12·00	0·200		12·65	0·072	
		27			70
12·30	0·192		12·75	0·065	
		40			47
12·40	0·188		12·90	0·058	
		50			33
12·50	0·183		13·20	0·048	
		140			18
12·55	0·176		13·70	0·039	
		1940			

TABLE II.

Titration of $K_2Cr_2O_7$ (0·0613 g.) mixed with 50 c.c. of KI (*N*/10) and 30 c.c. of H_2SO_4 (10*N*) against sodium sulphite (*N*/11·40).

Sodium sulphite.	E.M.F. (volts).	*E/C* (m.volts/c.c.).	Sodium sulphite.	E.M.F. (volts).	*E/C* (m.volts/c.c.).
13·00 c.c.	0·171		14·20	0·143	
		16			1660
13·50	0·163		14·25	0·060	
		20			120
13·90	0·155		14·30	0.051	
		25			80
14·10	0·150		14·40	0·046	
		40			50
14·15	0·148		14·60	0·036	
		100			30
			15·10	0·021	

TABLE III.

Titration of potassium ferricyanide (0·4109 g.) mixed with 25 c.c. of KI (2*N*) and 25 c.c. of HCl (5*N*) against sodium sulphite (*N*/9·72).

Sodium sulphite.	E.M.F. (volts).	*E/C* (m.volts c.c.).	Sodium sulphite.	E.M.F. (volts).	*E/C* (m.volts/c.c.).
11·00 c.c.	0·176		12·10	0·151	
		14			1640
11·50	0·169		12.15	0·060	
		20			120
11·70	0·165		12·20	0.063	
		25			60
11·90	0·160		12·30	0·057	
		30			35
12·00	0·157		12·50	0·050	
		40			28
12·05	0·155		13·00	0·036	
		80			16
			13·50	0·028	

TABLE IV.

Titration of $CuSO_4$, $5H_2O$ (0·2050 g.) mixed with 25 c.c. of KI (2 *N*) and 5 c.c. of H_2SO_4 (*N*) against sodium sulphite (*N*/11·36).

Sodium sulphite.	E. M. F. (volts).	*E/C* (m.volts/c.c.).	Sodium sulphite.	E. M. F. (volts).	*E/C* (m.volts/c.c.).
7·90 c.c.	0·204		9·35	0·072	
		16			80
8·40	0·196		9·40	0·068	
		24			60
8·90	0·184		9·45	0·065	
		35			50
9·10	0·177		9·55	0·060	
		50			25
9·20	0·172		9·75	0·055	
		60			18
9·25	0·169		10·25	0·046	
		60			12
9·30	0·166		10·75	0·040	
		1880			

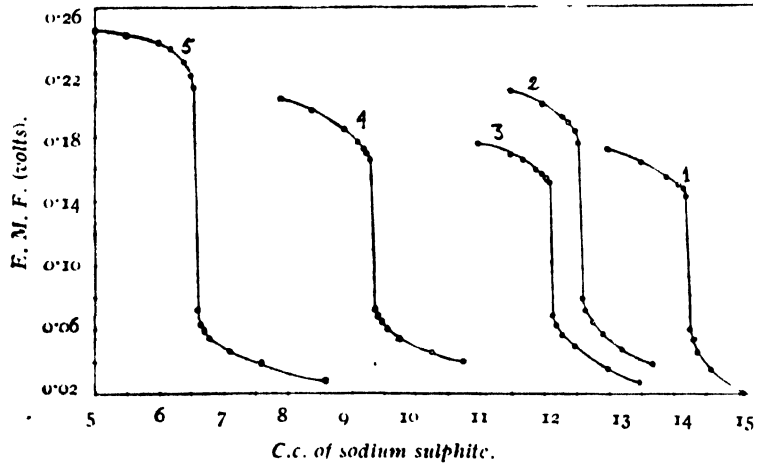
TABLE V.

Titration of H_2O_2 (25 c.c., 0·0275 *N*—0·0117 g.) mixed with 10 c.c. of H_2SO_4 (*N*) and 13 c.c. of KI (*N*) against sodium sulphite (*N*/9·60).

Sodium sulphite.	E. M. F. (volts).	*E/C* (m.volts/c.c.).	Sodium sulphite.	E. M. F. (volts).	*E/C* (m.volts/c.c.).
5·00 c.c.	0·247				
		6			
5·50	0·244				
		10			180
6·00	0·239		6·65	0·063	
		20			60
6·20	0·235		6·70	0·060	
		40			50
6·40	0·227		6·80	0·055	
		80			27
6·50	0·219		7·10	0·047	
		160			16
6·55	0·211		7·60	0·039	
		2780			11
6·60	0·072		8·60	0·028	

The curves for the above titrations are given in Fig. 1.

FIG. 1.



Curves 1—5 refer respectively to $K_2Cr_2O_7$, I_2, $K_3Fe(CN)_6$, $CuSO_4, 5H_2O$ and H_2O_2.

DISCUSSION.

With the addition of standard sodium sulphite solution, the E.M.F. decreased steadily till the equivalence point. At the equivalence point there was a sharp jump in potential in each case. For the addition of 0·05 c.c. of titrant, the inflection potential was of the order of 97, 83, 82, 94 and 139 millivolts for iodine, potassium dichromate, potassium ferricyanide, copper sulphate, and hydrogen peroxide respectively. After the equivalence point, there was again a fall in the potential which became steady on further addition of the reagent.

From the volume of the sodium sulphite solution required in each titration corresponding to the equivalence point, the amount of the substance was calculated. The values obtained are compared with the amounts of the substance taken as shown in Table VI.

TABLE VI.

Iodine		Potassium dichromate		Potassium ferricyanide	
Taken.	Found.	Taken.	Found.	Taken.	Found.
0·1586 g.	0·1584 g.	0·0613 g.	0·0612 g.	0·4109 g.	0·4108 g.
0·1921	0·1920	0·0971	0·0971	0·6322	0·6320
0·2230	0·2231	0·1245	0·1245	0·9271	0·9271
0·2514	0·2512	0·1688	0·1689	1·1244	1·1242

Copper sulphate		Hydrogen peroxide	
Taken.	Found.	Taken.	Found.
0·2050 g.	0·2051 g.	0·0117 g.	0·0116 g.
0·4382	0·4382	0·0328	0·0325
0·6917	0·6918	0·0574	0·0572
0·8543	0·8542	0.0765	0·0764

These results show that iodine, potassium dichromate, potassium ferricyanide, copper sulphate and hydrogen peroxide can be determined quantitatively by the potentiometric method.

We wish to express our best thanks to Prof. H. B. Dunnicliff for his kind interest in this work.

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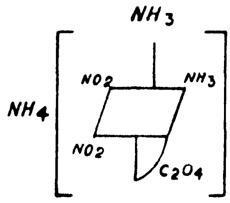
ON THE CONSTITUTION OF ERDMANN'S SALT. PART I.

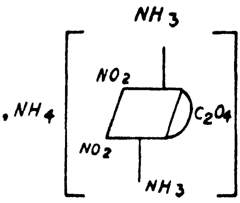
By Bhabes Chandra Ray.

As early as 1866 Erdmann described the ammonium tetranitro-diammine cobaltiate in which the two ammonium groups might have taken the two adjacent or remote positions yielding in the first case a '*cis*' and in the second a '*trans*' compound. The problem of determining the constitution of Erdmann's salt was taken up by Shibata and Maruki (*J. Coll. Sci. Imp. Univ. Tokio*, 1917, **41**, No. 2, 1). They prepared the oxalato-dinitro-diammine cobaltiate according to the method of Jorgensen. Theoretically this compound may have any of the following three constitutions.



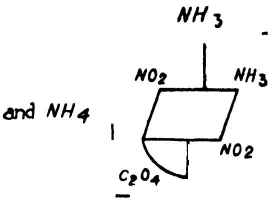
cis-Nitro-*cis*-ammonia.

(I)



cis-Nitro-*trans*-ammonia.

(II)



trans-Nitro-*cis*-ammonia.

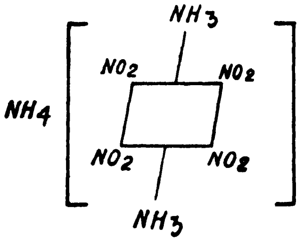
(III)

Shibata and Maruki (*loc. cit.*) claimed to have resolved the oxalato-dinitro-diammine salt, a fact from which it follows that (I) is its constitutional formula. Riesenfeld and Klement undertook the problem but could not resolve the compound. From this fact, as also from other chemical reactions they decided the original Erdmann's salt to have a *trans*-ammonia constitution (*Z. anorg. Chem.*, 1922, **124**, 1). Thomas (*J. Chem. Soc.*, 1923, **123** 617), however, prepared the oxalato-dinitro-diammine complex and, by fractional crystallisation separated two sets of crystals, (*i*) rhombohedral, the less soluble variety and (*ii*) monoclinic, the more soluble one. Thomas resolved the rhombohedral variety into its optical antipodes but could not separate the solid active form. The monoclinic variety could not be resolved and Thomas (*loc. cit.*) quite arbitrarily represented it by (III), without considering the possibility of the formation of (II).

In view of the contradictory statements regarding the resolvability of the oxalato-dinitro-diammino cobaltiate the works of the earlier authors were closely repeated. But neither the rhombohedral nor the monoclinic variety was found to be resolvable. Besides, the potassium salt from both the varieties on treatment with ethylenediamine, yielded the same insoluble non-electrolyte. This, however, supports Riesenfeld's view.

As a result of the study of absorption spectra, it has been generalised that where there is a pair of *trans*-nitro group in the cobaltammine complex, three distinct absorption bands appear in the spectrum at about 2000, 3000 and 4000 frequencies (expressed in terms of wave-number per mm.). The *cis*-nitro complexes, however, lack in the band at extreme ultra-violet the frequency of 4000 (Shibata, *J. Coll. Sci. Imp. Univ. Tokio*, 1915, **37**, No. 2, 1). The structure of the monoclinic variety was attempted to be determined from the standpoint of the above generalisation. It has been found to have a *cis*-nitro-*trans*-ammonia constitution like (II) (*vide* experimental).

From a careful consideration of the spectrographic and chemical evidences it appears that both rhombohedral as also the monoclinic varieties have identical structures, namely the *cis*-nitro and *trans*-ammonia groupings. The two sets of crystals would then indicate the allotropic modifications of the oxalato-dinitro-diammine cobaltiate. Thus assuming that during reactions no rearrangement of groups takes place, it can be well inferred that the original Erdmann salt is a *trans*-ammonia-*cis*-nitro compound and should be represented as :



(IV)

From measurements of crystal structure of the silver tetranitrodiammine cobaltiate by the X-ray method, Wells has shown recently that the two ammonia groups are in the *trans*-position (*Z. Krist.*, 1936, **95**, 74).

EXPERIMENTAL.

Barium Oxalato-dinitrodiammine Cobaltiate.—Two samples of ammonium oxalato-dinitro-diammine cobaltiate were prepared separately according to the methods of (*i*) Jorgensen (*Z. anorg. Chem.*, 1896, **11**, 440) and (*ii*) Riesenfeld and Klement (*loc. cit.*). The hot saturated solution of the ammonium salt was then treated with calculated quantity of barium chloride. On stirring the barium salt separated out. It was filtered, washed and recrystallised from water several times.

Fractional Crystallisation of the Barium Salt.—The barium salts were both subjected to fractional crystallisation whence a rhombohedral set of crystals formed the head and the monoclinic the tail fractions.

Reaction of Potassium Salt with Ethylenediamine.—To a solution of both the rhombohedral and monoclinic variety of the potassium salt, obtained from barium salt by treating the latter with potassium sulphate, ethylenediamine (just sufficient to replace the two ammonia molecules) was added. The solution was heated on a water-bath until the evolution of ammonia ceased. Insoluble brown precipitates containing ethylenediamine, nitrous acid, ammonia and cobaltic cobalt separated from both the rhombohedral as also the monoclinic variety. The salts were separately analysed and found to be identical. (Found : Co, 21·57 ; C_2O_4, 15·9. Reisenfeld and Klement's $Co_2En_2(NO_2)_4(NH_3)_2C_2O_4$ requires Co, 21·69 ; C_2O_4, 16·17 per cent).

Preparation of Strychnine Salt and Polarimetric Observation.—The barium salts of the complex cobaltiates were separately converted into strychnine sulphate and in each case the products were collected fractionally. Pure analysed samples of the strychnine salts of different fractions were tested in a polarimeter. Every sample gave exactly the same value for specific rotation (1% soln. in a 2 dm. tube $[\alpha]_D^{28^\circ}$, $-42{\cdot}5$). These different samples of strychnine salts were next treated with potassium iodide and after separation of strychnine iodide, the pure potassium salt was isolated (2 dm. of 1% solution of the potassium salt gave no rotation at all when tested polarimetrically).

Preparation of the Compound l-$[CoEn_3][Co(NO_2)_2C_2O_4(NH_3)_2]$, $6H_2O$.—To a saturated solution of the oxalato-dinitro-diammine cobaltiate was added a concentrated solution of the calculated quantity of *lævo* $(CoEn_3)Br_3$, $2H_2O$. Immediate precipitation of *l*-$CoEn_3$, $Co(NO_2)_2$, $C_2O_4(NH_3)_2$, $6H_2O$ occurred. The precipitate was filtered, washed, and recrystallised from hot water. (Found : Co, 20·31 ; NH_3, 8·71 ; Total N, 21·66. Calc. : Co, 20·24 ; NH_3. 8·74 ; Total N, 21·61 per cent.).

Polarimetric Investigation of the Salt.—The triethylenediammine base was precipitated with the help of a calculated quantity of $Na_5\left[Co\begin{matrix}(SO_3)_2\\(CN)_4\end{matrix}\right]$, $12H_2O$ and the precipitate immediately filtered by low suction. The residue was repeatedly washed with water, the filtrate and subsequent washings being collected in a measuring flask. The solution having a theoretical concentration of 1% was tested in a 2 dm. tube polarimetrically. Absolutely no rotation could be detected.

Constitution of the Monoclinic variety of Oxalato-dinitro-diammine Cobaltiate from Spectrographic Evidinces.—For comparing the validity of Shibata's generalisation with regard to the position of absorption maxima and the nitro groups, the ultra-violet absorption of the Flavo, Croceo and sodium cobaltinitrite etc., have been studied, in addition to those of the rhombohedral and monoclinic varieties of the oxalato-dinitro complexes.

Conc. $=N/10,000$. Time of exposure = 20 sec. for soln. ; 10 sec. for arc ; 5 sec. for scale.

Arc used—Iron Arc.

(Observations made by varying the length of columns in Baly's Tube)

Substance.	Absorption band between.	Wave-number per mm	Substance.	Absorption band between.	Wave-number per mm.
Na-cobaltinitrite	2640-2650Å	3781	Erdmann's salt	2430-2450Å	4099
	3320-3350	2999		3320-3350	2999
	4700-4800	2105		4650-4700	2139
cis-Dinitro-tetrammine	Absent		Oxalato-dinitro-diammine (prepared accordtng to Riesenfeld's method)	Absent	
	3320-3350	2990		3320-3350	2999
	4650-4700	2139		4700-4800	2103
trans-Dinitro tetrammine			Oxalato-dinitro-diammine (rhombohedral)	Absent	
	2430-2450	4099		3320-3350	2999
	3320-3340	3003		4700-4800	2103
	4650-4700	2139	Oxalato-dinitro diammine (monoclinic)	Absent	
				3320-3350	2999
				4700-4800	2103

In conclusion the author wishes to express his grateful thanks to Dr. P. B. Sarkar for his kind interest in the work and facilities of his laboratory.

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ON THE ATOMIC SUSCEPTIBILITY OF DIVALENT COPPER.

By S. S. Bhatnagar, H. Lessheim, and Mohan Lal Khanna.

The susceptibilities of the various cupric salts were measured with the help of Gouy's balance. The sample was placed in a tube between the poles of a strong electro-magnet and the force exerted by the magnet was measured by means of an analytical balance. In those cases, in which the measurements had to be taken at various temperatures, a furnace made of nichrome wire on mica plates was placed between the poles of the magnet and the balance was standardised separately for every temperature employed. The temperatures were taken by a standard thermometer reading tenths of a degree Centrigrade.

Cupric Fluoride (anhydrous).

CuF_2.

Temp.	$\chi \times 10^6$.	$\chi_M \times 10^6$.	$\chi_A \times 10^6$.	$1/\chi_A$ Obs.	$1/\chi_A$ Calc.	C_m.	μ.	θ.
305·5°K	15·191	1542·9	1554·9	643·13	643·13	0·4052	1·80	+45·6
328·4	14·004	1422·4	1434·4	697·15	697·12			
347·5	13·135	1334·1	1346·1	743·45	744·03			
368·2	12·258	1246·3	1258·3	794·73	794·50			
383·0	11·725	1190·9	1202·9	831·32	831·21			
403·0	11·062	1123·5	1135·5	881·04	881·04			

The reduction of the molar susceptibility to the atomic one for copper was done by deducting Pascal's value (*cf.* Stoner, "Magnetism and Matter", 1934, p. 470) of -6×10^{-6} for fluorine. The perfect agreement between the measured atomic susceptibilities and the calculated ones show that the Weiss-Curie law is strictly obeyed.

The Curie temperature is $\theta = +45·6°K$, the Curie constant is 0·4052, giving 1·8 Bohr magnetons for copper in CuF_2.

Cupric Hydro-arsenite.

$CuHAsO_3$.

Temp.	$\chi \times 10^6$.	$\chi_M \times 10^6$.	$\chi_A \times 10^6$.	$1/\chi_A$.		C_m.	μ.	θ
				Obs.	Calc.			
304·5°K	6·827	1280·4	1334·5	749·34	749·34	0·4956	2·00	−67·0
328·3	6·401	1200·5	1254·6	797·08	797·36			
336·1	6·282	1178·1	1232·2	811·56	813·10			
347·5	6·090	1142·0	1196·1	836·04	836·10			
357·2	5·949	1115·6	1169·7	854·89	855·66			
368·1	5·787	1085·3	1139·4	877·66	877·66			

The atomic susceptibility was obtained from the molar one by employing Kido's value (*Sci. Rep. Tohoku Imp. Univ.*, 1933, **22**, 835) of $-51·20 \times 10^{-6}$ for the arsenite radical and Pascal's value (*loc. cit.*)of $-2·95 \times 10^{-6}$ for hydrogen. The observed and the calculated values are again in accord with each other. The Curie temperature is $\theta = -67·0°K$, the Curie constant, 0·4956, corresponding to 2·0 Bohr magnetons.

Cupric Ortho-arsenate.

$Cu_3(AsO_4)_2 \cdot 4H_2O$.

Temp.	$\chi \times 10^6$.	$\chi_M \times 10^6$.	$\chi_A \times 10^6$.	$1/\chi_A$		C_m.	μ.	θ.
				Obs.	Calc.			
304·3°K	7·593	4105·5	1423·0	702·48	702·48	0·4695	1·945	−24·3
328·1	7·062	3818·5	1327·9	753·05	753·17			
335·9	6·908	3734·9	1300·1	769·18	769·79			
347·3	6·681	3612·5	1259·3	794·08	794·07			
358·3	6·490	3509·1	1224·8	816·45	817·50			
368·4	6·307	3410·3	1191·9	839·02	839·02			

The molar susceptibility was reduced to the atomic one with the help of Kido's value (*loc. cit.*) of $-56{\cdot}7 \times 10^{-6}$ for the arsenate radical and Pascal's value of $-13{\cdot}0 \times 10^{-6}$ (*loc. cit*) for the water of crystallization. The Curie temperature is $\theta = -24{\cdot}3°K$, the Curie constant, 0·4695, from which $\mu =$ 1·95 Bohr magnetons.

Other Cupric Compounds.

The following cupric salts were measured at only one temperature (17C°) in order to obtain their magneton numbers; measurements at several temperatures were not possible, because the salts decomposed. Effective magneton numbers were calculated under the assumption of the validity of Curie's law. The values obtained from the various compounds are in as good an accord with each other as can be expected under the circumstances.

Compound	Temp.	$\chi \times 10^6$.	$\chi_M \times 10^6$.	$\chi_A \times 10^6$.	$\mu_{eff.}$
$Cu(HCOO)_2$	290°K	8·80	1351·6	1385·6	1·80
$CuCl_2{\cdot}2KCl$	290	4·75	1347·1	1464·2	1·85
$CuCl_2{\cdot}2NH_4Cl{\cdot}2H_2O$	290	5·31	1473·5	1608·1	1·94
$CuCl_2{\cdot}2NH_3$.	290	8·27	1394·0	1463·0	1·85
$[Cu(NH_3)_4]SO_4{\cdot}H_2O$	290	5·70	1400·9	1505·1	1·88
$[Cu(NH_3)_4](NO_3)_2$	290	5·62	1437·1	1523·1	1·89

The compounds investigated are most probably all of them co-valent, but for the following discussion this is immaterial; the situation is precisely the same for electro-valent or co-valent linkage.

Two of the electrons of the copper atom form diamagnetic combinations with the valency electrons of the negative radical, and the resulting paramagnetism is due to a core of the copper atom with 27 electrons in $d^9\ {}^2D_{5/2}$.

Theoretically (Van Vleck, "Electric and Magnetic Susceptibilities", Oxford, 1932, Chapter XI) the number of Bohr magnetons should be given by the equation,

$$\mu = \sqrt{4S(S+1) + L(L+1)}$$

from which for a ^{2}D term μ = 3·0 Bohr magnetons. On the other hand, if according to Van Vleck's theory the orbital moment is quenched, one should obtain

$$\mu = \sqrt{4S(S+1)}$$

which yields μ = 1·73 Bohr magnetons.

The values obtained here vary between 1·8 and 2·0 magnetons. In consideration of the fact that some uncertainty as regards the correction due to the negative radical cannot be avoided, these values are in a good enough agreement with each other and show, that in the case of cupric salts the orbital magnetic moment is almost completely quenched and that in accordance with the results of Klemm and Schüth (*Z. Electrochem.*, 1932, **38**, 621) there is no difference in the magnetic state of the copper atom either in simple or in complex compounds. At the same time the values are fully in accord with those obtained by other authors (*cf.* table in Sugden, *J. Chem. Soc.*, 1932, 164).

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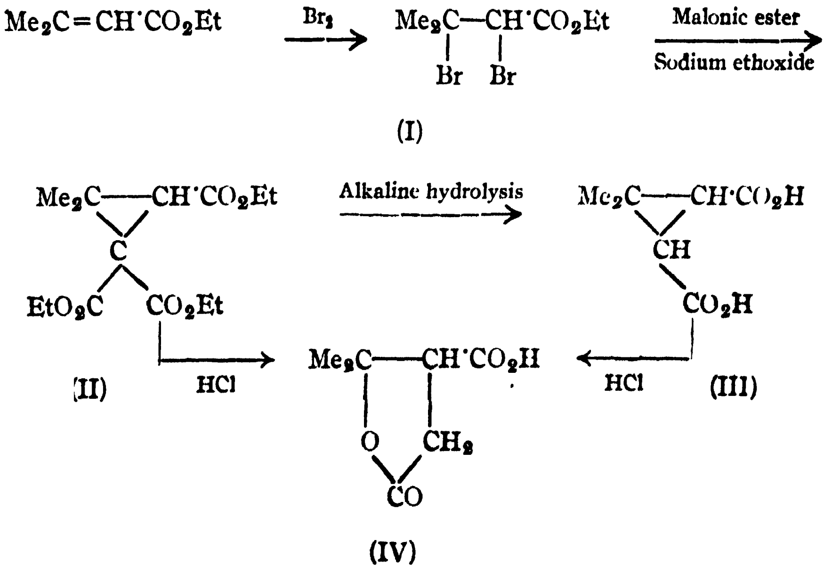
A NEW SYNTHESIS OF CARONIC ACID.

By Ranajit Ghosh.

Caronic acid has been synthesised by Perkin and Thorpe (*J. Chem. Soc.*, 1899, **75**, 48), Kotz (*J. pr. Chem.*, 1907, *ii*, **75**, 501), Farmer and Ingold (*J. Chem. Soc.*, 1920, **117**, 1362), Kon and co-workers (*ibid.*, 1921, **119**, 1316) and recently by Guha and Saukaran (*Current Science*, 1937, **5**, 388).

The present papers describes another synthesis of caronic acid by the following method : Ethyl αβ-dibromo-ββ-dimethylpropionate (I), prepared from ethyl ββ-dimethylacrylate (Prentice, *Annalen*, 1896, **292**, 273) was allowed to react with ethyl malonate in presence of sodium ethoxide, when ethyl 2:2-dimethyl*cyclo*propane-1:1:1′-tricarboxylate (II) was obtained. The ester on hydrolysis with alcoholic potash gave the tricarboxylic acid which was slowly heated to 200° when it lost carbon dioxide and passed into the caronic acids (III). The caronic acids were separated according to the method of Perkin and Thorpe (*loc. cit.*). The hydrolysis of the ester (II) with hydrochloric acid was, however, attended with the formation of terebic acid (IV), probably *via* caronic acid, conversion of which into terebic acid in presence of halogen acids is well known.



It may be mentioned here that *cis*-caronic acid has been isolated in good yield by this method, the amount of *trans*-caronic acid formed simultaneously being very small.

EXPERIMENTAL.

Preparation of Ethyl 2:2-Dimethylcyclopropane-1:1:1'-tricarboxylate (II).—Ethyl malonote (34 g.) was added in the cold to the solution obtained by dissolving sodium (5 g.) in absolute alcohol (70 c. c.). Ethyl αβ-dibromo-ββ-dimethylpropionate (30 g.) was slowly added to the mixture and the reaction flask was cooled in a current of ice-cold water. When the addition of the dibromo ester was complete, the reaction was allowed to proceed under reflux on the water-bath for 3 hours. The alcohol was then distilled off as far as possible and the residual mass was treated with water and extracted with ether. The ethereal solution was washed with water, dried over calcium chloride and distilled in vacuum after removal of ether. After a considerable amount of malonic ester was distilled off, a colourless oil, which after repeated fractionation boils at 142-46°/5 mm., and at 153°/9 mm., was collected. [Found : C, 58·6 ; H, 7·9 ; M. W. (cryoscopic in benzene), 280. $C_{14}H_{22}O_6$ requires C, 58·7 ; H, 7·7 per cent. M. W., 286].

Alkaline Hydrolysis of (II) *: Isolation of Caronic Acids* (III).—The above tricarboxylic ester (10 g.) was treated with alcoholic potash (10 g. in 100 c.c. of ethyl alcohol) and refluxed on a water-bath for 12 hours. Alcohol was then removed as far as possible and the residual mass treated with water. The alkaline solution was extracted with ether. The aqueous alkaline solution was then acidified with hydrochloric acid and extracted with ether. The ethereal layer on drying with anhydrous sodium sulphate and distillation left a residue which solidified on keeping. The whole of the residue was slowly heated to 200° during which carbon dioxide was eliminated. The mass was then treated with excess of aqueous ammonia and evaporated to dryness. The dried ammonium salt was extracted with alcohol leaving a small amount (A) insoluble in the solvent. The alcoholic solution was treated with ether and the precipitate collected, dissolved in water, acidified and extracted several times with ether. The ether solution on evaporation left a residue which when crystallised from water melted at 176° (*cis*-caronic acid, m. p. 176°). (Found : C, 52·96 ; H, 6·42. Calc. for $C_7H_{10}O_4$: C, 53·16 ; H, 6·33 per cent). The properties of synthetic *cis*-caronic acid are identical with those described by Bayer (*loc. cit.*) and Perkin and Thorpe (*loc. cit.*).

trans-Caronic Acid.—The insoluble portion (A) mentioned above was dissolved in water, the solution acidified with hydrochloric acid and repeatedly extracted with ether. The ethereal solution was then evaporated and the residue crystallised from water, m. p. 213°. (*trans*-caronic acid, m. p. 213°). (Found: C, 53·01; H, 6·47. Calc. for $C_7H_{10}O_4$: C, 53·16; H, 6·33 per cent).

Acid Hydrolysis of (II) : *Isolation of Terebic Acid* (IV).—The tricarboxylic ester (5 g.) was boiled with hydrochloric acid (*d* 1·19, 30 c.c.) and the solution was evaporated to dryness. The residue was crystallised from water, m. p. 174°. [Found : C, 53·2 ; H, 6·4 ; Equiv. (in the cold), 156. $C_7H_{10}O_4$ requires C, 53·16; H, 6·3 per cent. Equiv., 158). The ammonium salt of this acid in alcohol cannot be precipitated by ether.

Action of Hydrochloric Acid on cis- *and* trans-*Caronic Acids.*—The acids were separately boiled with hydrochloric acid (*d* 1·19) and the resulting product was isolated as above. The acids melt at 174° and a mixture with terebic acid from the above experiment had the same m. p. A mixture of terebic acid obtained by these methods and caronic acid, however, melted at a lower temperature.

In conclusion I wish to express my sincere thanks to Sir P. C. Rây, for his kind interest in this investigation and for placing the resources of his laboratory at my disposal.

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EFFECT OF THE SIMULTANEOUS ACTION OF RADIATIONS OF DIFFERENT FREQUENCIES ON THE BROMINATION OF CINNAMIC ACID AND STILBENE.

By J. C. Ghosh, S. K. Bhattacharyya and M. L. Narasimha Murthi.

The simultaneous action of radiations of different frequencies on photochemical reactions has already been studied in many cases and the results so far obtained may be classified into three groups:

(*i*) Reactions in which the simultaneous action of radiations of different frequencies produce an effect which is equal to the sum of the effects of the individual radiations, *e.g.*, the oxidation of quinine by chromic acid studied by Luther and Forbes (*J. Amer. Chem. Soc.*, 1909, **31**, 770) and the bromination of toluene by Bruner and Czarnecki (*Bull. Acad. Sci. Cracow*, 1910, 516).

(*ii*) In a fairly large number of cases it has been found, however, that the combined effect of two radiations is less than the sum of the individual effects. This has been encountered in the bromination of cinnamic acid in carbon tetrachloride, alcohol and benzene solutions, studied by Plotnikow (*Z. physikal. Chem.*, 1912, **79**, 641), in the photochemical oxidation of hydriodic acid by oxygen in aqueous solutions by Padoa and Miss Vita (*Gazzetta*, 1924, **54**, 147), and in the oxidation of oxalic acid by ferric chloride by the latter authors. They have also observed the diminished effect in the bromination of cinnamic acid in chloroform and carbon tetrachloride solutions (*Trans. Faraday Soc.*, 1925, **21**, 573) and in the absorption of carbon dioxide by green plant (*Gazzetta*, 1928, **58**, 647). Recently Ghosh and Bhattacharyya (*Z. physikal. Chem.*, 1936, **B 31**, 420) have shown that in the oxidation of mandelic acid by bromine the combined effect of two radiations is less than the sum of the individual effects.

(*iii*) As examples of reaction, where the combined effect of two radiations is greater than that given by the additive rule, may be mentioned the photosynthesis of hydrochloric acid by Padoa (*Z. physikal. Chem.*, 1926, **120**, 202), the isomeric transformation of *o*-nitrobenzaldehyde to *o*-nitrosobenzoic acid by Weigert and Kummerer (*Ber.*, 1913, **46**, 1207), and the photolysis of potassium ferric oxalate by Allmand and Webb (*J. Chem. Soc.*, 1929, 1518), the decompositon of ammonia by Kuhn (*Compt. rend.*, 1923, **177**, 956) and the reactions between iodide and various salts of sodium and potassium, and between oxalic acid and chromic acid, potassium permanganate, and between bromine and sodium potassium tartrate studied by Mukherjee and Dhar (*J. Phys. Chem*, 1929, **33**, 850). But a quantitative explanation of the observed results has rarely been attempted. In the oxidation of mandelic acid by bromine, Ghosh and Bhattacharyya (*loc. cit.*) have established a definite relationship between the combined effect and the individual effects of two radiations of different frequencies.

The object of the present investigation is to find out whether any definite relationship exists between the combined effect and the individual effects of two radiations of different frequencies in the bromination of cinnamic acid and also stilbene. The kinetics of the bromination of cinnamic acid and stilbene in 546$\mu\mu$ and 536$\mu\mu$ were studied by Berthoud (*Trans. Faraday Soc.*, 1925, **21**, 554), and notably by Ghosh and Purkayastha (*J. Indian Chem. Soc.*, 1925, **2**, 261 ; 1927, **4**, 409, 553). These photochemical reactions are peculiar in some respects. They are unimolecular with respect to bromine but there is a slight diminution in the value of the velocity constant with increase in time.

EXPERIMENTAL.

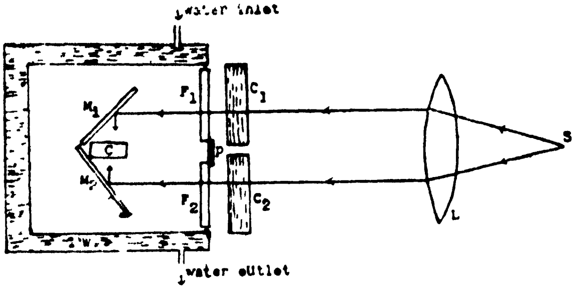
The source of radiation was a quartz mercury point-o-lite lamp, run at a constant current of 2·3 amperes and at a constant voltage of 35 volts. A parallel beam of light was obtained by placing a convex lens at its focal length from the lamp. The reaction cell (1·5 cm. × 1·5 cm. × 0·5 cm. in the case of cinnamic acid and 1·8 cm. × 1·8 cm. × 0·5 cm. in the case of stilbene) made of plane glass plates fused into one another with a stopper at the top, was placed inside a double jacketted metal box with two windows side by side, one for the passage of light of one frequency, and the other for light of a different frequency. The temperature was kept constant by passing, with the aid of a circulating pump, water from a thermostat through the annular space of the box. The light beam was passed through the glass cells C_1 and C_2, each 2 cm. thick, containing a 2% solution of copper sulphate to cut off the heat rays and then through the filters F_1 and F_2 for making the light monochromatic. The following filters were used :

(*i*) for 406$\mu\mu$: mercury violet
(*ii*) for 436$\mu\mu$: Zeiss monochromatic blue filter C
(*iii*) for 546$\mu\mu$: Schott and Gen Green VGI.

For intensity variation "Nitra glass" filters were used.

The following arrangement was adopted for the simultaneous action of two radiations of different frequencies on the reaction mixture contained in the reaction cell. A beam of light passing through the filters C_1 and F_1 was reflected by a plane glass miror M_1 at an angle of 45° and then passed through the stoppered rectangular cell C Similarly a beam of light of a different frequency passing initially through the filters C_2 and F_2 (through the other window of the metal box) was reflected on to the reaction cell by the mirror M_2. The relative positions of the mirrors and the reaction cell are closely shown in Fig. 1.

FIG. 1.



C—Reaction cell, C_1, C_2—$CuSO_4$ filters, F_1, F_2—monochromatic filters;
S—quartz point-o lite lamp, W—double jacketted metal box

The intensity of the absorbed radiation was measured by means of a Moll thermopile and Moll galvanometer calibrated by means of a standard lamp supplied by the "Bureau of Standards". The intensity of the incident radiation was found by observing the deflections produced by the monochromatic radiation after passing through the solvent alone. The intensity of the absorbed radiation was calculated from the data of the molecular extinction coefficient of bromine found by Ghosh and Bhattacharyya (*Z. physikal. Chem.*, 1936, **B 32**, 145). ϵ (molecular extinction coefficient) as found by them is 26·5 for 546$\mu\mu$, 131·1 for 436$\mu\mu$, and 130·5 for 406$\mu\mu$.

Merck's 'extra pure' cinnamic acid and Schuchardt's pure stilbene further purified by crystallisation were used. The bromine was also of Merck's extra pure "Reagent" variety. For making solutions Merck's extra pure CCl_4 further purified by distillation over fused $CaCl_2$ was used.

The velocity of reaction was determined by pipetting out 0·27 c.c. of the reaction mixture and titrating iodometrically with 0·01*M*-thiosulphate by means of a microburette. The reactions were all carried out at 31°.

The compositions of the reaction mixtures used in this investigation are identical with those used by Ghosh and Purkayastha (*J. Indian Chem. Soc.*, 1927, **4**, 409).

All the experiments in this investigation were finished within one hour of the exposure. During this period there is no dark reaction between bromine and cinnamic acid or stilbene.

The Light Reactions.

The kinetics of the reactions were studied in three monochromatic radiations 546, 436 and 406$\mu\mu$ individually and under the simultaneous action of two radiations, violet (406$\mu\mu$) and blue (436$\mu\mu$), violet (406$\mu\mu$) and green (546$\mu\mu$), and blue (436$\mu\mu$) and green (546$\mu\mu$). The velocity constants are all calculated as unimolecular constants.

$$k = \frac{2\cdot3}{t} \log_{10} \frac{a}{a-x}\ .$$

The experimental results are tabulated in Tables I and II. The significance of each column will be found from the discussion. In the tables below, I is the light energy absorbed per sq. cm. per second by the bromine molecules. K is the unimolecular velocity constant.

$$\mathrm{Vi} = 406\mu\mu,\ \mathrm{Bl} = 436\mu\mu,\ \mathrm{Gr} = 546\mu\mu,\ E = Nh\nu.$$

From the Tables I and II it will be found that

(*a*) The combined effect of two radiations is always less than the sum of the two individual effects.

(*b*) The velocity constant in pure monochromatic radiation varies as the square root of the intensity of absorbed radiation.

DISCUSSION.

In the photobromination of cinnamic acid and stilbene in CCl_4 solution, the velocity of reaction for single monochromatic radiation (λ_1) can be deduced from the following equations postulated by Ghosh (*Z. physikal. Chem.*, 1930, **B9**, 155).

$$\begin{array}{lcllll}
Br_2 + E_{\lambda_1} & = & 2Br_{\lambda_1} & & & \\
Br_{\lambda_1} + Br_{\lambda_1} & = & Br_2 & \cdots & \cdots & (i) \\
Br_{\lambda_1} + Br_2 & = & Br_{3_{\lambda_1}} & \cdots & \cdots & (ii) \\
Br_{3_{\lambda_1}} & = & Br_{\lambda_1} + Br_2 & \cdots & \cdots & (iii) \\
Br_{3_{\lambda_1}} + A & = & ABr_2 + Br_{\lambda_1} & \cdots & \cdots & (iv)
\end{array}$$

In these reactions the concentration of Br_{λ_1} atom per c.c. in the stationary state is given by

$$\mathrm{Br}_{\lambda_1} = \frac{1}{\sqrt{K_1}} \cdot \sqrt{\frac{I_{\lambda_1}}{E_{\lambda_1}}}.$$

Hence $$-\frac{1}{[\mathrm{Br}_2]} \cdot \frac{d[\mathrm{Br}_2]}{dt}$$

$$= \frac{K_4 A}{K_3 + K_4 A} \cdot K_2 \cdot \frac{1}{\sqrt{K_1}} \cdot \sqrt{\frac{I_{\lambda_1}}{E_{\lambda_1}}} = K_{\lambda_1} \text{ (observed).}$$

We assume that every collision between two Br atoms leads to the formation of a molecule of bromine in presence of an inert solvent molecule, and hence K_1 is independent of the nature of the radiation which causes photo-dissociation of the molecules of bromine into atoms ; but that velocity constants K_2, K_3, K_4, which are subsequent dark processes, depend on the energy content of the bromine atoms which initiate the reaction chain.

We shall use the symbols,

$$\mathrm{Br}_{\lambda_1} = \frac{K_4 A}{K_3 + K_4 A} . K_2 \text{ for } \lambda_1 ;$$

$$\frac{I_{\lambda_1}}{E_{\lambda_1}} = V_1, \qquad \mathrm{Br}_{\lambda_1} = n_1$$

or $$\mathrm{Br}_{\lambda_1} = K_{\lambda_1} . \sqrt{K_1} . \frac{1}{\sqrt{V_1}}.$$

For simultaneous action of two radiations λ_1 and λ_2,

$$n_1 + n_2 = \mathrm{Br}_{\lambda_1} + \mathrm{Br}_{\lambda_2}$$

$$= \frac{1}{\sqrt{K_1}} \left[\frac{I_{\lambda_1}}{E_{\lambda_1}} + \frac{I_{\lambda_2}}{E_{\lambda_2}} \right]^{\frac{1}{2}}$$

$$= \frac{1}{\sqrt{K_1}} . [V_1 + V_2]^{\frac{1}{2}} \qquad \ldots \text{ (a)}$$

Again,

Rate of formation of $\mathrm{Br}_{\lambda_1} = \frac{I_{\lambda_1}}{E_{\lambda_1}}$.

Rate of disappearance of $\mathrm{Br}_{\lambda_1} = K_1[\mathrm{Br}^2_{\lambda_1} + \mathrm{Br}_{\lambda_1} . \mathrm{Br}_{\lambda_2}]$

$$= K_1[n_1{}^2 + n_1 . n_2]$$

That is, $V_1 = K_1[n_1{}^2 + n_1 . n_2]$

Similarly, $V_2 = K_1[n_2{}^2 + n_1 . n_2]$

Solving for $\frac{n_1}{n_2}$, we get,

$$\frac{n_1}{n_2} = \frac{1}{2}\left\{ -\left(\frac{V_2 - V_1}{V_2}\right) \pm \sqrt{\left(-\frac{V_2 - V_1}{V_2}\right) + 4 . \frac{V_1}{V_2}} \right\} \quad \ldots \quad (\beta)$$

Hence n_1 and n_2 are known from equations (α) and (β) taking the positive values.

The velocity constant due to the simultaneous action of two radiations λ_1 and λ_2 is given by

$$-\frac{1}{[\mathrm{Br}_2]} . \frac{d[\mathrm{Br}_2]}{dt} = K_{\lambda_1 . \lambda_2} = \mathrm{Br}_{\lambda_1} n_1 + \mathrm{Br}_{\lambda_2} n_2 .$$

$$= K_{\lambda_1} . \sqrt{K_1} . \frac{1}{\sqrt{V_1}} . n_1 + K_{\lambda_2} \sqrt{K_1} . \frac{1}{\sqrt{V_2}} . n_2$$

where K_{λ_1} = observed velocity constant under the influence of monochromatic radiation λ_1,

K_{λ_2} = observed velocity constant under the influence of radiation λ_2.

In the columns X and XI of Tables I and II are given the calculated and experimentally found velocity constants. They agree very well within the limits of experimental error and this justifies the mechanism of reaction which has been developed above.

TABLE I

Cinnamic Acid.

Conc. of cinnamic acid = 0·024M.
" " " bromine = 0·0204M.

	I	II	III	IV	V	VI	VII	VIII	IX	X	XI
	I_1.	$\sqrt{\frac{I_1}{E_{\lambda_1}}}\times 10^6$.	$K_{\lambda_1}\times 10^4$.	$\frac{K_{\lambda_1}}{\sqrt{I_1/E_{\lambda_1}}}$.	I_2.	$\sqrt{\frac{I_2}{E_{\lambda_2}}}\times 10^6$.	$K_{\lambda_2}\times 10^4$.	$\frac{K_{\lambda_2}}{\sqrt{I_2/E_{\lambda_2}}}$	$\sqrt{\frac{I_1}{E_{\lambda_1}}+\frac{I_2}{E_{\lambda_2}}}$	$K_3\times 10^4 = K_{\lambda_1+\lambda_2}\times 10^4$ Calc.	Found.
		(Bl)			(Gr)					(Bl + Gr.)	
(a)	94·9	5·868	2·23	38·00	132·9	7·788	2·02	25·94	9·746	2·96	3·16
(b)	94·9	5·868	2·23	38·00	46·9	4·62	1·29	27·93	7·467	2.55	2·65
(c)	94·9	5·868	2·23	38·00	24·4	3·333	0·87	26·10	6·748	2·37	2·23
(d)	32·3	3·423	1·06	30·96	132·9	7·788	2·02	25·94	8·507	2·28	2·44
(e)	32·3	3·423	1·06	30·96	24·4	3·333	0·87	26·10	4·777	1·37	1·71
(f)	16·2	2·42	0·88	36·37	132·9	7·788	2·02	25·94	8·149	2·19	2·18
(g)	16·2	2·42	0·88	36·37	46·9	4·62	1·29	27·93	5·217	1·55	1·54
(h)	50·2	4·267	1·59	37·27	240	10·47	2·745	26·22	11·3	2·92	3·33
(i)	50·2	4.267	1·59	37·27	80	6·033	1·637	27·13	7·39	2·11	2·40
(j)	50·2	4·267	1·59	37 27	40	4·266	1·127	26·41	6·033	1·92	2·23
(k)	16·7	2·463	0·93	37·77	240	10·47	2·745	26·22	10·52	2·82	3·13
(l)	8·4	1·744	0·575	32·98	240	10·47	2·745	26·22	10·6	2·87	2·78

TABLE I (*contd.*).

	(Gr)				(Vi)					(Gr + Vi)	
(a)	240	10·47	2·745	26·22	42·5	3·807	1·3	34·14	11·13	3·02	3·15
(b)	80	6·033	1·637	27·13	42·5	3·807	1·3	34·14	7·136	2·08	2·23
(c)	40	4·266	1·127	26·41	42·5	3·807	1·3	34·14	5·719	1·70	1·92
(d)	240	10·47	2·745	26·22	14·2	2·198	0·72	32·75	10·68	2·96	2·83
(e)	40	4·266	1·127	26·41	14·2	2·198	0·72	32·75	4·799	1·33	1·70
(f)	132·9	7·788	2·01	25·81	42·5	3·807	1·3	34·14	8·66	2·38	2·67
(g)	50·9	4·297	1·40	32·58	42·5	3·807	1·3	34·14	5·741	1·91	2·05
(h)	25·5	3·087	0·94	30·45	42·5	3·807	1·3	34·14	4·906	1·68	1·71
(i)	132·9	7·788	2·01	25·81	14·2	2·198	0·72	32·75	8·091	2·13	2·35
(j)	25·5	3·087	0·98	30·45	14·2	2·198	0·72	32·75	3·796	1·19	1·31

	(Vi)				(Bl)					(Vi + Bl)	
(a)	42·5	3·807	1·3	34·14	114	6·363	2·40	37·71	7·473	2·75	2·36
(b)	42·5	3·807	1·3	34·14	38	3·713	1·48	39·87	5·318	1·96	1·85
(c)	42·5	3·807	1·3	34·14	19	2·625	1·1	41·91	4·625	1·69	1·47
(d)	14·2	2·198	0·72	32·75	114	6·363	2·40	37·71	6·795	2·53	2·19
(e)	14·2	2·198	0·72	32·75	19	2·625	1·1	41·91	3·424	1·31	1·08

TABLE II

Stilbene.

Conc. of stilbene = 0·024M. Conc. of bromine = 0·0216M.

	I	II	III	IV	V	VI	VII	VIII	IX	X	XI
	I_1	$\sqrt{\frac{I_1}{E_{\lambda_1}}} \times 10^6$.	$K_{\lambda_1} \times 10^4$.	$\frac{K_{\lambda_1}}{\sqrt{I_1} E_{\lambda_1}}$.	I_2.	$\sqrt{\frac{I_2}{E_{\lambda_2}}} \times 10^6$.	$K_{\lambda_2} \times 10^4$.	$\frac{K_{\lambda_2}}{\sqrt{I_2} E_{\lambda_2}}$.	$\sqrt{\frac{I_1}{E_{\lambda_1}} + \frac{I_2}{E_{\lambda_2}}}$.	$K_3 \times 10^4 = K_{\lambda_1+\lambda_2} \times 10^4$ Calc.	Found.
	(Gr)				(Bl)					(Gr + Bl)	
(a)	64·8	5·43	2·455	45·22	94	5·841	3·187	54·56	7·977	4·01	3·96
(b)	64·8	5·43	2·455	45·22	31·4	3·372	1·97	58·42	6·39	3·12	2·99
(c)	64·8	5·43	2·455	45·22	15·7	2·384	1·307	54·81	5·93	2·77	2·76
(d)	21·6	3·135	1·39	44·34	94	5·841	3·187	54·56	6·63	3·466	3·24
(e)	21·6	3·135	1·39	44·34	15·7	2·384	1·307	54·81	3·941	1·90	1·87
(f)	10·8	2·217	1·003	45·23	94	5·841	3·187	54·56	6·247	3·34	3·23
(g)	10·8	2·217	1·003	45·23	31·4	3·372	1·97	58·42	4·049	2·22	2·10

TABLE II (*contd.*).

	(Bl)				(Vi)					(Bl + Vi)	
(*a*)	94	5·841	3·187	54·56	64·7	4·708	1·65	35·05	7·501	3·52	3·47
b)	31·4	3·372	1·97	58·42	64·7	4·708	1·65	35·05	5·79	2·49	2·7
(*c*)	15·7	2·384	1·307	54·81	64·7	4·708	1·65	35·05	5·277	2·06	1·75
(*d*)	94	5·841	3·187	54·56	21·6	2·716	1·05	38·67	6·44	3·33	3·14
(*e*)	15·7	2·384	1·307	54·81	21·6	2·716	1·05	38·67	3·615	1·65	1·56
	94	5·841	3·187	54·56	11·0	1·921	0·80	41·65	6·149	3·278	3·08
	31·4	3·372	1·97	58·42	11·0	1·921	0·80	41·65	3·881	2·00	1·86

(Vi)				(Gr)					(Vi + Gr)	
64·7	4·708	1·66	35·05	64·8	5·43	2·455	45·22	7·186	2·94	3·22
64·7	4·708	1·66	35·05	21·6	3·135	1·39	44·34	5·656	2·14	2·16
64·7	4·708	1·66	35·05	10·8	2·217	1·003	45·23	5·204	1·92	1·94
21·6	2·716	1·06	38·67	64·8	5·43	2·455	45·22	6·071	2·66	2·77
21·6	2·716	1·06	38·67	10·8	2·217	1·003	45·23	3·505	1·45	1·30
11·0	1·921	0·80	41·65	64·8	5·43	2·455	45·22	5·759	2·58	2·70
11·0	1·921	0·80	41·65	21·6	3·135	1·39	44·34	3·676	1·66	1·46

Application of Einstein's Law of Photochemical Equivalence.

The calculation of the quantum efficiency has not much theoretical significance in these reactions; because the quantum efficiency has got a very high value and also the temperature coefficient is very large. These points have been discussed by Ghosh and Purkayastha (*loc. cit.*). The quantum efficiency has been calculated here only to have some idea of the mechanism of the reactions. In Table III the quantum efficiency in different wave-lengths has been tabulated.

A typical calculation is given below:—

Wave-length $= 436\mu\mu$.

With 0·024*M*-cinnamic acid and 0·0206*M*-Br_2, the change in concentration of Br_2 in 25 minutes was 0·00655*M*. The reaction cell is 0·5 cm. thick and 1·5 × 1·5 sq. cm. in area. The energy absorbed per sq. cm. per sec. = 114 ergs. Total number of quanta of blue light absorbed per sec.

$$= \frac{114 \times 436 \times 10^{-7} \times 1{\cdot}5 \times 1{\cdot}5}{6{\cdot}5 \times 10^{-27} \times 3 \times 10^{10}} = 7{\cdot}46 \times 10^{13}.$$

Total number of molecules transformed per second

$$= \frac{0{\cdot}5 \times 1{\cdot}5 \times 1{\cdot}5 \times 0{\cdot}00655 \times 6{\cdot}06 \times 10^{23}}{1000 \times 25 \times 60} = 297{\cdot}7 \times 10^{13}$$

$$\therefore \gamma \text{ (quantum efficiency)} = \frac{297{\cdot}7 \times 10^{13}}{7{\cdot}46 \times 10^{13}} = 40.$$

In the following table the compositions of the reaction mixtures are similar to those used in Tables I and II. *I* is the intensity of radiation absorbed by bromine in ergs per sq. cm. per second, γ is the quantum efficiency.

TABLE III.

	Cinnamic acid.		Stilbene.	
λ.	*I*.	γ.	*I*.	γ.
$406\mu\mu$	42·5	72	64·7	61·2
	14·2	127	21·6	125
			10·8	208
$436\mu\mu$	114	40	94	71
	50·2	63·5	31·4	144
	32·3	84·8	15·7	214
	16·2	132·5		
$546\mu\mu$	240	15·6	64·8	48·7
	132	24·8	21·6	135
	80	32·6	10·8	176
	24·4	68·6		

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SYNTHESIS OF O-CYANOALDEHYDES. PART I.

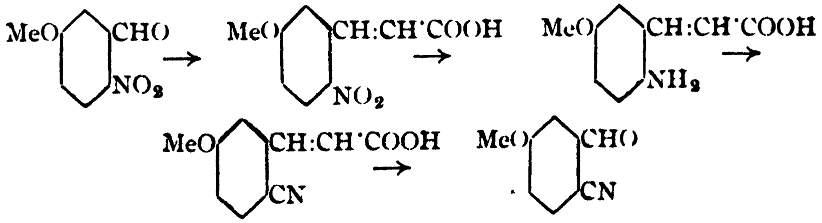
By S. N. Chakravarti and K. Ganapati.

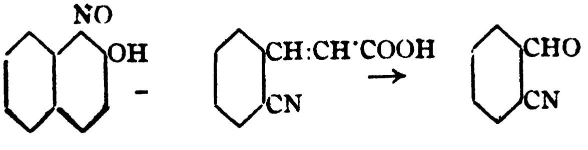
None of the *o*-cyanoaldehydes have yet been synthesised, and in this paper we record our attempts to synthesise this important class of compounds which were required during the course of synthetical experiments in the group of alkaloids.

Attempts to convert *o*-aminobenzaldehydes into *o*-cyanoaldehydes by Sandmeyer's reaction under a large variety of different conditions were unsuccessful. The diazotisation of amines did not proceed smoothly and clear diazo solution was not obtained in any case under the usual conditions.

It was thought that the reaction might go better if the aldehyde group were first protected, but preliminary experiments to convert *o*-amino-Schiff's bases, oximes and acetals to the corresponding cyanoaldehydes were all unsuccessful. The chief difficulty lay in the diazotisation which could only be accomplished in strong acids. The scheme involving the use of the *o*-aminoaldoximes seemed to be particularly attractive as itwas found that these amino-oximes could readily be prepared in almost quantitative yields from the corresponding nitro compounds (*vide* experimental part). The diazotisation of the *o*-aminoaldoximes could also be readily effected in strong hydrochloric acid solution, but the replacement of the diazo group by the cyano group could not be effected. Under one set of conditions azido-aldehydes were formed (*cf*. *Ber*., 1901, **34**, 1331; 1927, **60**, 1741).

It was eventually found that the *o*-cyanoaldehydes could be obtained readily although only in poor yields (about 15%) by oxidation (with permanganate) of *o*-cyanocinamic acids which could be synthesised readily in excellent yields from *o*-nitro-aldehydes and by other methods. *o*-Cyanobenzaldehyde (m. p. 76°) and 3-methoxy-6-cyanobenzaldehyde (m.p. 107°) were thus synthesised.





o-Aminocinnamic acids can be converted into the corresponding *o*-cyanocinnamic acids in excellent yields. Oxidation of the *o*-cyanocinnamic acids by means of permanganate in presence of benzene takes a varied course, the main product in each case being a high melting sparingly soluble substance. Attempts are being made to improve the yield of *o*-cyanoaldehydes by the action of other oxidising agents like ozone, nitrogen peroxide on *o*-cyanocinnamic acids.

Synthesis of other methoxy-*o*-cyanoaldehydes and dimethoxy-*o*-cyanoaldehydes is reserved for a future communication.

EXPERIMENTAL.

2-Amino-3-methoxybenzaldoxime.—*m*-Hydroxybenzaldehyde was methylated by means of dimethyl sulphate in alkaline solution in an yield of about 90% (Chakravarti, Vaidyanathan and Venkatasubban, *J. Indian Chem. Soc.*, 1932, **9**, 574) and then nitrated under conditions similar to those used by Ayling, Hinkel and Morgan (*J. Chem. Soc.*, 1932, 1115). 2-Nitro-3-methoxybenzaldehyde which was thus formed in about 95% yield was purified by repeated crystallisations from benzene and was converted into its oxime in the following manner: The aldehyde (1·6 g.) was dissolved in the least amount of alcohol and treated with a solution of hydroxylamine hydrochloride (1·03 g.) and sodium hydroxide (1·2 g.) in water and the whole allowed to remain for 24 hours. On acidifying the oxime was precipitated in quantitative yield. It was crystallised from alcohol, m.p. 170°.

The oxime (10 g.) was dissolved in sodium hydroxide solution (5 g. in 50 c. c. of water) and added to freshly precipitated ferrous hydroxide from ferrous sulphate (85·5 g. in 50 c.c. of water) and sodium hydroxide (26·3 g. in water). The reduction was carried out in the cold in alkaline medium. The whole was well stirred, filtered and the precipitate washed several times with cold water. The filtrate (along with the washings) was then saturated with carbon dioxide when the amine-oxime was precipitated in an yield of over 80%. On recrystallisation from methyl alcohol it melted at 136-37°. (Found: N, 17·0. $C_8H_{10}O_2N_2$ requires N, 16·9 per cent).

6-Amino-2 : 3-dimethoxybenzaldoxime.— 6-Nitro-2 : 3-dimethoxybenzaldehyde was prepared from *o*-vanillin by the method previously described (Chakravarti, *J. Indian Chem. Soc.*, 1929, **6**, 215) and converted into the oxime thus :—The aldehyde (2·1 g.) was dissolved in alcohol and treated with a solution of hydroxylamine hydrochloride (1 g.) and sodium hydroxide (1·2 g.) in water. The mixture was allowed to stand for 24 hours and then just acidified with acetic acid when the oxime was precipitated in quantitative yield. The oxime crystallises in needles from alcohol, m.p. 137°. (Found : N, 12·6. $C_9H_{10}O_5N_2$ requires N, 12·4 per cent).

The oxime (4·6 g.) was dissolved in sodium hydroxide solution (2 g. in 20 c.c. of water) and the solution added to the precipitate obtained from crystallised ferrous sulphate (33·8 g.) and sodium hydroxide (10·5 g. in 200 c.c. of water). The whole was vigorously shaken for about 1/4 hour and then the ferric hydroxide filtered, washed several times with cold water. The filtrate and washings were saturated with carbon dioxide when the amino-oxime was precipitated in an excellent yield. It crystallises from methyl alcohol in shining plates, m.p. 147°. (Found : N, 14.5. $C_9H_{12}O_3N_2$ requires N, 14·3 per cent).

Diazotisation and replacement of the diazo group by the cyano group of 2-amino-3-methoxybenzaldoxime and 6-amino-2 : 3-dimethoxybenzaldoxime were tried under the following conditions :—

(*i*) Diazotisation and replacement of the diazo groups under the usual conditions.

(*ii*) Diazotisation in presence of excess of concentrated hydrochloric acid at -5°, neutralisation of the free acid by sodium hydroxide, barium hydroxide or sodium carbonate solution and subsequent treatment with cuprous cyanide under the usual conditions.

(*iii*) Diazotisation of the amines in presence of excess of strong mineral acid, the diazo solution and alkali being added at the same time to the cuprous cyanide, keeping the cyanide solution just alkaline throughout the reaction.

Although diazotisation did seem to proceed in (*ii*) and (*iii*), cyano compounds could not be obtained under any of the conditions. Under conditions (*ii*) and (*iii*) 2-azido-aldehydes were formed and these are being further investigated.

6-*Amino-3-methoxycinnamic Acid.*—*m*-Hydroxybenzaldehyde was nitrated and 6-nitro-3-hydroxybenzaldehyde separated by the method of Friedlander and Schenck (*Ber.*, 1914, **47**, 3046). 6-Nitro-3-hydroxybenzaldehyde was methylated by means of dimethyl sulphate in alkaline solution and the methoxy compound converted into 6-nitro-3-methoxycinnamic acid (m.p. 227°) in almost quantitative yield by malonic acid-pyridine method. A solution of 6-nitro-3-methoxycinnamic acid (11·6 g.) in dilute ammonia was added to a solution of ferrous sulphate (106 g. in 150 c.c. of water). To the mixture heated on the steam-bath was then gradually added concentrated ammonia (42 c.c.) while the contents were vigorously shaken throughout. After all the ammonia had been added, the whole was further heated for 1/4 hour, filtered, the filtrate concentrated down to one third its volume and then carefully made just acid. The amino-acid was precipitated as a crystalline yellow powder, m.p. 186°, yield 70%. The hydrochloride crystallised from water in prismatic needles, m.p. 204° (decomp.). (Found : C, 52·1 ; H, 5·3. $C_{10}H_{12}O_3NCl$ requires C, 52·3 ; H, 5·2 per cent).

6-Cyano-3-methoxycinnamic Acid.—A mixture of 6-amino-3- methoxycinnamic acid (7 g.), water (45 c.c.) and concentrated hydrochloric acid (10 g.) was cooled to 0° and diazotised with a solution of sodium nitrite (3·4 g.). The clear diazo solution was added to a hot solution of potassium cuprous cyanide, obtained by adding a solution of potassium cyanide (12·6 g. in 22 c.c. of water) to a solution of copper sulphate (11g. in 67 c.c. of water). The whole was heated on the water-bath for one hour, cooled and acidified. The precipitated cyano-acid was filtered, washed and dissolved in dilute sodium carbonate solution. The sodium carbonate solution was acidified with concentrated hydrochloric acid. The precipitated cyano-acid was filtered, washed and recrystallised from methyl alcohol (charcoal) in long clusters of needles, m.p. 220°. (Found : C, 64·8 ; H, 4·2. $C_{11}H_9O_3N$ requires C, 65·0 ; H, 4·4 per cent).

6-Cyano-3-methoxybenzaldehyde.—A solution of 6-cyano-3-methoxycinnamic acid (2·5 g.) in sodium carbonate solution was covered with benzene (300 c.c.) in a separating funnel and a cold saturated solution of potassium permanganate (4·2 g.) was gradually added with vigorous shaking. After all the permanganate had been added the mixture was further shaken for 15 minutes, filtered and the precipitate washed several times with small quantities of benzene. The benzene layer was separated from the aqueous layer of the filtrate, dried over anhydrous sodium sulphate. It was then concentrated to about 30 c.c. when a crystalline substance (A) (0·65 g.) separated, which on repeated crystallisation from benzene was obtained as prismatic needles, m.p. 218°. The mother liquors from (A) on further concentration deposited first more of the substance (A) and then 6-cyano-3-methoxybenzaldehyde, which was readily separated, the aldehyde being much more soluble in benzene. The latter on repeated crystallisation from alcohol was obtained in clusters of needles, m.p. 107°. (Found : C, 67·2 ; H, 4·3. $C_9H_7O_2N$ requires C, 67·1 ; H, 4·4 per cent).

The substance (A) could not be readily hydrolysed.

From the aqueous layer of the filtrate on concentration and acidification a mixture of the starting acid and a new acid (m.p. about 132°) was precipitated.

o-Cyanocinnamic acid was prepared from α-nitroso-β-naphthol by Beckmann's transformation (Edward, *J. Chem. Soc.*, 1926, 815).

o-Cyanobenzaldehyde.—*o*-Cyanocinnamic acid was oxidised under conditions similar to those described above for 6-cyano-3-methoxycinnamic acid. From the benzene layer at first a sparingly soluble substance crystallising in needles, m.p. 227°, separated and then *o* cyanobenzaldehyde, which on repeated crystallisation melted at 76°. (Found : C, 73·0; H, 3·7. C_8H_5ON requires C, 73·3 ; H, 3·8 per cent). From the aqueous layer, the starting acid, *o*-cyanobenzoic acid and an acid (m.p. 197-202°) were isolated.

2-Amino-3-methoxycinnamic Acid.— 12 G. of 2-nitro-3-methoxycinnamic acid (which was synthesised from 2-nitro-3-methoxybenzaldehyde by the malonic acid-pyridine method) dissolved in dilute ammonia were added to a solution of ferrous sulphate (106 g. in 150 c.c. of water) which had been heated on the water-bath to about 90°. Ammonia (45 c.c.) was then added gradually with vigorous shaking and after all the addition, heating and shaking were continued for further 15 minutes. The whole was then filtered, precipitated, washed several times with dilute ammonia and the filtrate and washings concentrated to one fourth of its bulk and then made just acid when 2-amino-3-methoxycinnamic acid was precipitated, yield 50%. It crystallised from water in yellow glittering prisms, m.p. 189° (decomp.). (Found : C, 62·2 ; H, 6·0. $C_{10}H_{11}O_3N$ requires C, 62·2 ; H, 5·7 per cent).

2-Cyano-3-methoxycinnamic Acid.—A mixture of 2-amino-3-methoxycinnamic acid (3·5 g.), water (23 c.c.) and concentrated hydrochloric acid (5 c.c.) was cooled to 0° and diazotised with a solution of sodium nitrite (1·7 g). The clear diazo solution was added to a hot solution of potassium cuprous cyanide obtained by adding to a solution of copper sulphate (5·5 g. in 34 c.c. of water) a solution of potassium cyanide (6·3 g. in 11 c.c. of water). The whole was heated on the water-bath for 1 hour, cooled and acidified when crude cyano-acid was precipitated which was filtered, washed and then dissolved in dilute sodium carbonate solution and acidified with concentrated hydrochloric acid. The precipitated cyano-acid was filtered, washed and crystallised from alcohol or acetone (charcoal). It crystallised in needles, m.p. 149 . (Found : C, 64·7 ; H, 4·3. $C_{11}H_9O_3N$ requires C, 65·0 ; H, 4·4 per cent).

Yields in this series are lower than in the corresponding 6-cyano series due probably to increased steric difficulty, both the *ortho* positions to the nitro or amino group being occupied.

Experiments on the oxidation of 2-cyano-3-methoxycinnamic acid are in progress.

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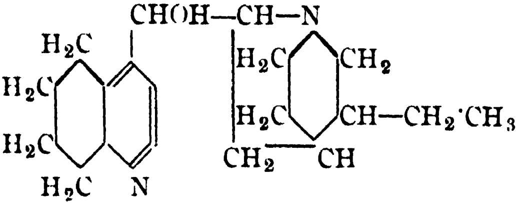
ACRIDINE DERIVATIVES AS ANTIMALARIALS.

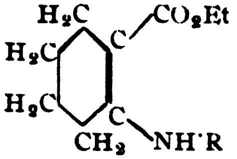
By U. P. Basu and S. J. Das-Gupta.

Since the observation of Mauss and Mietzsch (*Klin-Woch.*, 1933, **12**, 1276) that the dihydrochloride of 2-chloro-5 (ω-diethylamino*iso*amyl)-amino-7-methoxyacridine, better known as 'Atebrin,' has a powerful action on all asexual forms of the malarial parasites, a good deal of attention (*cf.* Magidson and Grigorovski, *Ber.*, 1936, **69**, 396, 537) has been given to the syntheses of various other acridine derivatives of the above type, having particularly a dialkylaminoalkylamino side-chain in position 5. In view of the fact that reduction generally diminishes the toxicity of a compound and that the Bz-tetrahydrohydrocinchonine (I) has the same influence on the fever as the cinchonine itself (*cf.* Braunn and Lemke, *Annalen*, 1930, **478**, 176), a study on the physiological activity of a hydrated acridine derivative of the above type was considered to be of special interest. As very little is known about the chemistry of hydrated acridines, a method was found out for their synthesis and several compounds of the above type have been prepared.



(I)

It was shown by Sen and Basu (*J. Indian Chem. Soc.*, 1930, **7**, 435) that ethyl *cyclo*hexanone-2-carboxylate when treated with an aromatic amine at the room temperature afforded an anil (II), which may be readily converted into a tetrahydroacridone (III). This reaction has been utilised for the syntheses of various 1:2:3:4-tetrahydro-5-chloroacridine derivatives of the type (IV, R=Cl). When these chloro compounds are treated with phenol they easily afford the phenoxy derivatives (IV, R=OPh) from which several 5-dialkylaminoacridines [IV, $R=NH(CH_2)_nNEt_2$] have been obtained. It has also been noted that the aminoacridine [IV, $R=NH\ (CH_2)_n\ NEt_2$] might be more conveniently obtained from 5-chloroacridine itself. In fact, this process has been usually followed in the course of this investigation. The aminoacridines are almost colourless and readily form stable dihydrochlorides which are highly soluble in water and extremely bitter in taste.



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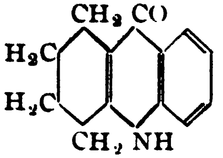

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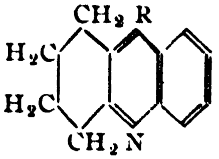


(IV)

EXPERIMENTAL.

1 : 2 : 3 : 4-*Tetrahydro-5-chloroacridine* (IV, R = Cl).—Equimolecular quantities of ethyl *cyclo*hexanone-2-carboxylate and aniline were mixed and kept in a vacuum desiccator over fused calcium chloride for 8-10 days. The mixture was then heated at 250-260° for about 2 hours, and the residual mass on cooling was washed with ether and collected. It was 1 : 2 : 3 : 4-tetrahydroacridone (III), m. p. 358-60° (*cf.* Sen and Basu, *loc. cit.*). To a mixture of Bz-tetrahydroacridone (4 g.) and finely powdered phosphorus pentachloride (5 g.), a few c.c. of phosphorus oxychloride was added just in sufficient quantity to make a thin paste and the whole was slowly heated to 120-130° and this temperature was maintained for about 2 hours when most of the phosphorus oxychloride distilled over. The contents in the flask solidified. It was well cooled and decomposed with ice, filtered and the filtrate made alkaline with ammonia. The precipitate was filtered off, washed and crystallised from petroleum ether, m. p. 68-69°. (Found : Cl, 16·63. Calc. for $C_{13}H_{12}NCl$: Cl, 16·32 per cent). This compound has been described by Perkin and Sedgwick (*J. Chem. Soc.*, 1924, **125**, 2446) to melt at 226° ; and by Braun and others (*Ber.*, 1931, **64**, 227) to melt at 68°.

1:2:3:4-*Tetrahydro-5-phenoxyacridine* (IV, R = OPh).—To a hot solution of phenol (3 g.) in caustic potash (0·3 g.) 1:2:3:4-tetrahydro-5-chloroacridine (0·5 g.) was added slowly and the mixture was heated in an oil-bath at 140° for about 2 hours. The hot melt was poured into about 50 c.c. of 10% caustic soda solution and kept overnight. The supernatant liquid was decanted off and the residual mass was triturated with 5% caustic soda solution, filtered and washed free from alkali. The crude phenoxy compound separated from petroleum ether in microscopic needles, m. p. 102 . It was converted to its hydrochloride by passing dry hydrochloric acid gas into its ethereal solution and crystallised from a mixture of alcohol and ether (1 : 1), m. p. 223-25°. (Found : Cl, 11·53. $C_{19}H_{17}ON, HCl$ requires Cl, 11·40 per cent).

1 : 2 : 3 : 4 - *Tetrahydro*- 5 (*δ- diethylaminobutyl)aminoacridine.*—The above tetrahydrochloroacridine (0·6 g.) was heated in a sealed tube with 0·8 g. of diethylaminobutylamine and a little copper powder at 150-160° for several hours. The mass was treated with water and the supernatant layer was decanted off. It was thus repeatedly washed with water in order to remove the unreacted amine. The residual semi-solid mass was extracted with ether, the ethereal solution was filtered and treated with dilute acetic acid. The acetic acid solution was made alkaline with ammonia in the cold when the base separated as a semi-solid mass which was again washed several times with water. It was once more extracted with ether, the ethereal solution dried over anhydrous potassium carbonate and treated with dry hydrochloric acid gas. The dihydrochloride thus obtained being extremely hygroscopic could not be isolated. Its aqueous solution was accordingly treated with a solution of sodium salt of methylenedioxynaphthoic acid in the cold when a salt of the aminoacridine with methylenedioxynaphthoic acid was isolated in a crystalline form. It was collected and thoroughly washed. It is tasteless and insoluble in water, m. p. 216-20°. (Found: N, 5·56. $C_{21}H_{31}N_3$, $C_{23}H_{16}O_6$ requires N, 5·88 per cent).

7- *Methoxy*- 1 : 2 : 3 : 4-*tetrahydroacridone.*—A mixture of ethyl *cyclo*hexanone-2-carboxylate (17 g.) and *p*-anisidine (12·3 g.) was left overnight. There was much turbidity owing to the separation of water from the reaction mixture and it was left in vacuum over fused calcium chloride for 10 days, when a clear dark solution was obtained. It was then heated in an oil-bath at 260-270° for about 2 hours when the contents of the flask solidified. On cooling the solid product was treated with ether and was filtered, yield 18 g. The compound crystallised from alcohol in prismatic needles, m. p. 295°. It is soluble in dilute mineral acids. (Found: N, 6·29. $C_{14}H_{15}O_2N$ requires N, 6·10 per cent).

7-*Methoxy*-5-*chloro*-1 : 2 : 3 : 4-*tetrahydroacridine* was prepared from the above acridone (4 g.) and finely powdered phosphorus pentachloride (5 g.) as in the case of (IV, R = Cl). It separated in pale yellow prismatic needles from dilute alcohol, m. p. 122°. (Found: Cl, 15·01. $C_{14}H_{14}ONCl$ requires Cl, 14·34 per cent).

7-*Methoxy*-5-*phenoxy*-1 : 2 : 3 : 4-*tetrahydroacridine.*—The chloroacridine (2 g.) was heated with phenol (8 g.) at 140-150° for about 3 hours. The reaction mixture was then poured into a *N*-NaOH solution when the phenoxy derivative separated as an oil. It was left overnight when it solidified. The supernatant liquid was decanted off and it was triturated with caustic soda solution, filtered and washed free from alkali. It crystallises from petroleum ether in long prismatic needles, m.p. 120°. (Found: N, 5·2. $C_{20}H_{19}O_2N$ requires N, 4·6 per cent). It is a crystalline solid and readily dissolves in dilute acids. On passing dry hydrogen chloride to its ethereal solution the hydrochloride was easily obtained, which melted to a green liquid at 220 (decomp.). (Found: Cl, 10·13. $C_{20}H_{19}O_2$ N, HCl requires Cl, 10·4 per cent).

It forms a picrate, m.p. 190-192°. When treated with δ-diethylaminobutylamine in a sealed tube at 150-160° it affords the 5-aminoacridine derivative which is also easily obtained by the method described below.

Dihydrochloride of 7-Methoxy-1 : 2 . 3 : 4-tetrahydro-5-(δ-diethylaminobutyl)-aminoacridine.—7-Methoxy-1.2 : 3 : 4-tetrahydro-5-chloroacridine (0·6 g.) was heated with δ-diethylaminobutylamine (0·8 g.) and a little copper powder at 160° for several hours. The mixture was treated as in the previous case. The ethereal solution finally obtained was dried over anhydrous potassium carbonate and treated with dry hydrogen chloride. The crude dihydrochloride was crystallised from a mixture of absolute alcohol and dry ether and the product was rapidly dried in a vacuum desiccator, m.p. 193-94 . (Found : Cl, 16·31. $C_{22}H_{33}ON_3$, 2HCl requires Cl, 16·59 per cent).

Dihydrochloride of 7-Methoxy-1 : 2 : 3 : 4-tetrahydro-5-(γ-diethylaminopropyl)- aminoacridine.—The chloro compound (0·6 g.) was heated with γ-diethylaminopropylamine (0·8 g.) in a sealed tube at about 160° with a little copper powder. After the usual treatment of the reaction mixture the dihydrochloride was isolated and crystallised from a mixture of alcohol and ether and rapidly dried, m.p. 228-29 . [Found . Cl, 16·3. $C_{21}H_{31}ON_3$, 2HCl, H_2O requires Cl, 16·44 per cent Found (in sample dried at 105-110°): N, 10·24 ; Cl, 17·02. $C_{21}H_{31}ON_3$, 2HCl requires N, 10·15; Cl, 17·15 per cent].

7-Methoxy-2-methyl-1 : 2 : 3 : 4-tetrahydroacridone.—Molecular proportions of ethyl 5-methyl*cyclo*hexanone-2-carboxylate and *p*-anisidine were mixed together and left over as usual. On heating the reaction mixture at 250-260°, the contents of the flask set to a crystalline solid which was collected, washed with ether and finally crystallised from glacial acetic acid, m.p. 335°. (Found : N, 5·89. $C_{15}H_{17}O_2N$ requires N, 5·76 per cent).

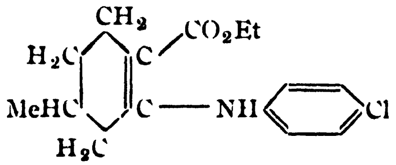
7-Methoxy-2-methyl-1 : 2 : 3 : 4-tetrahydro-5-chloroacridine.—The acridone derivative was heated with a mixture of phosphorus penta- and oxychloride at 120-30° as in the formation of the previous chloroacridine. The solid residue on treatment with ice and ammonia afforded a yellow substance which on crystallisation from methyl alcohol separated in slender needles, m.p. 90°. (Found : Cl, 13·70. $C_{15}H_{16}ONCl$ requires Cl, 13·58 per cent).

7-Methoxy-2-methyl-1 : 2 : 3 : 4-tetrahydro-5-phenoxyacridine, was prepared by heating the chloroacridine (2 g.) with phenol (8 g.) as in the previous case. It crystallised from petroleum ether in long prismatic needles, m.p. 103°. (Found : N, 4·56. $C_{21}H_{21}O_2N$ requires N, 4·38 per cent).

Dihydrochloride of 7-Methoxy-2-methyl-1 : 2 : 3 : 4-tetrahydro-5-(δ-diethylaminobutyl)- aminoacridine.—The chloroacridine (0·7 g.) was heated with δ-diethylaminobutylamine (0·8 g.) in a sealed tube with a trace of copper powder at 160° as usual. The dihydrochloride was isolated in the usual manner and crystallised from a mixture of alcohol and ether and dried in vacuum, m.p. 203-4° The substance was dried at 110 and analysed. (Found : N, 9·08 $C_{23}H_{35}ON_3$, 2HCl requires N, 9·5 per cent).

Dihydrochloride of 7-Methoxy-2-methyl-1 : 2 : 3 : 4-tetrahydro-5-(γ-diethylaminopropyl) aminoacridine.—The chloroacridine (0·8 g.) was heated with diethylaminopropylamine (0·8 g.) at 150-160° in a sealed tube with a little copper powder. After usual treatment the dihydrochloride was isolated and cryslallised, m.p. 242-43°. [Found. Cl, 15·80. $C_{22}H_{33}ON_3$, 2HCl, H_2O requires Cl, 15·92 per cent. Found (in a sample dried at 110°) : N, 9·86; Cl, 16·51. $C_{22}H_{33}ON_3$, 2HCl requires N, 9·81; Cl, 16·59 per cent.]

*Ethyl 2-(4′-chloroanilido)-4-methyl-Δ^1-*cyclo*hexene-1-carboxylate.*



The carboxylate derivative of *m*-methyl*cyclo*hexanone was mixed with a molecular proportion of *p*-chloroaniline and kept in a desiccator in *vacuo*. Gradually crystals began to separate. These were collected and crystallised from dilute alcohol in fine prismatic needles, m.p. 90°. (Found : N, 4·90. $C_{16}H_{20}O_2NCl$ requires N, 4·77 per cent).

7-Chloro-2-methyl-1 : 2 : 3 : 4-tetrahydroacridone.—The above anilido compound was heated in an oil-bath at 270° for ½ hour when the contents in the flask solidified to a crystalline mass. This was cooled, washed with alcohol and crystallised from boiling glacial acetic acid. It is sparingly soluble in the common organic solvents and melts with decomposition at 375° in a sealed capillary. (Found : N, 5·38. $C_{14}H_{14}ONCl$ requires N, 5·65 per cent).

5 : 7-*Dichloro-2-methyl-1 : 2 : 3 : 4-tetrahydroacridine*.—The acridone derivative was made into a paste with phosphorus penta-and oxychloride and heated as usual. The reacted mass was further treated with hydrochloric acid and the whole was filtered. The filtrate was cooled and neutralised with ammonia. A semi-solid mass was isolated which was left over in a refrigerator. Next day the solid found was collected and crystallised from methyl alcohol (charcoal), m.p. 89°. (Found: Cl, 26·44. $C_{14}H_{13}NCl_2$ requires Cl, 26·69 per cent).

7-*Chloro-1 : 2 : 3 : 4-tetrahydroacridone*.—This acridone derivative was obtained in the usual way from the reaction mixture obtained by mixing ethyl *cyclo*hexanone-2-carboxylate and *p*-chloroanil (1 : 1) at the room temperature and keeping the mixture over fused calcium chloride in *vacuo* for about a fortnight. The substance was difficultly soluble in alcohol. It crystallised from a large volume of the same solvent in silky needles, m.p. 380°* (Found : Cl, 15·22. $C_{13}H_{12}ONCl$ requires Cl, 15·20 per cent).

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* This compound has been synthesised in another way and found to melt at 385° by Prof. Dr. O. J. Magidson of Scientific Chemical-Pharmaceutical Research Institute, Moscow, U. S. S. R. (*private communication*).

THE PHENYLTHIOCARBAMIDES. A CONTRIBUTION TO THE STUDY OF THE TRIAD -N·C·S-. PART IV. THE ACTION OF AQUEOUS SILVER NITRATE ON PHENYLTHIOCARBAMIDE

By Kunj Behari Lal and Hans Krall.

Phenylthiocarbamide interferes with the estimation of thiocyanic acid by Volhard's method. The objects of the present investigation are to see how silver nitrate interacts with phenylthiocarbamide in acid solution, and to determine the conditions in which Volhard's method can be used to estimate thiocyanic acid in the presence of thiocarbamide.

By the interaction of aqueous solutions of phenylthiocarbamide and silver nitrate, a white precipitate is obtained which is stable in presence of dilute nitric acid. Analytical results indicate the formation of several complexes of these two compounds which vary in composition with the proportion of the reagents used. The complex having the largest proportion of silver nitrate is formed when an aqueous solution of phenylthiocarbamide is treated with moderate excess of silver nitrate. It is certainly not a silver derivative but appears to be a complex (1: 1), although it usually takes up 10-12% extra silver nitrate, a fact which indicates the existence of still higher complexes. By using less silver nitrate lower complexes are obtained which appear to be of less interest. The monomolecular complex reacts with potassium thiocyanate changing to phenylthiocarbamide-silver thiocyanate. The latter is also formed directly by the interaction of phenylthiocarbamide and silver thiocyanate or of phenylthiocarbamide, silver nitrate and potassium thiocyanate.

These complex formations may be represented as follows :

$$\mathrm{PhNHCSNH_2 + AgNO_3 = PhNHCSNH_2 \cdot AgNO_3} \qquad (i)$$

$$\mathrm{PhNHCSNH_2 \cdot AgNO_3 + KSCN = PhNHCSNH_2 \cdot AgSCN + KNO_3} \qquad (ii)$$

$$\mathrm{PhNHCSNH_2 + AgSCN = PhNHCSNH_2, \cdot AgSCN} \qquad (iii)$$

$$\mathrm{PhNHCSNH_2 + AgNO_3 + KSCN = PhNHCSNH_2 \cdot AgSCN + KNO_3} \qquad (iv)$$

Volhard's method, using excess of silver nitrate and titrating back with standard potassium thiocyanate, can be used to estimate thiocyanic acid provided that the phenylthiocarbamide present is less in molecular proportions than the thiocyanic acid. Ten molecular proportions of phenylthiocarbamide correspond to eleven of silver nitrate.

EXPERIMENTAL.

Expt. 1. *Action of Aqueous Silver Nitrate on Phenylthiocarbamide in presence of a Variable quantity of Nitric Acid.*—The variable amount of nitric acid was added to 50 c.c. of $N/50$-phenylthiocarbamide solution in 4% alcohol (the solubility in water alone is very low) followed by 15 c.c. of $N/10$- silver nitrate drop by drop with shaking; after a minute or so it was filtered, washed with dilute nitric acid (2%) and the filtrate titrated back with $N/10$-potassium thiocyanate, using 5 c.c. of 5% ferric alum as indicator. The results are recorded in Table I.

TABLE I.

$2N$-HNO_3 (c.c.)	...	0·3	0·5	1	2	3	4	6	8	10	20
$AgNO_3$ used up (c.c.)	...	11	11·1	11·1	11	11	11	11	11	10·9	9·5

Below 2 c.c. and above 8 c.c. the interaction was more or less incomplete but within this range uniform results were obtained and we have, therefore, in all our experiments used 5 c.c. of $2N$-nitric acid for every 100 c.c. of solution.

It will be noted that 50 c.c. of phenylthiocarbamide solution took up 11 c.c. of silver nitrate, whereas one equivalent is 10 c.c. Discussion of this phenomenon would be out of place but it may be mentioned that we have found that

(*i*) the excess of silver nitrate can be removed by suspending the precipitate in dilute nitric acid;

(*ii*) it is not a case of adsorption;

(*iii*) as little as 5 c.c. of silver nitrate remove all the phenylthiocarbamide from solution with the formation of a different complex;

(*iv*) in aqueous solutions the excess of nitrate taken up is never more than 10-12% of the equivalent ;

(*v*) in alcoholic solutions complexes richer in silver nitrate are formed.

Expt. 2. *Examination of the Phenylthiocarbamide—Silver nitrate Complex obtained in the Above Experiment.*—Heated on a nickel foil it exploded evolving voluminous yellow fumes. Decomposition occurred at 132-34°. Hot water, ammonia and alkalis decomposed it readily, but it could be recrystallised with slight decomposition from dilute nitric acid. It interacted slowly with potassium thiocyanate solution (*vide infra*).

1·61 G. of the substance, suspended in absolute alcohol (50 c.c.) and treated with hydrogen sulphide, gave silver sulphide (Ag, 33·08 per cent). The alcoholic solution gave a copious precipitate with nitron acetate showing that the complex contained nitrate, while on evaporation to dryness it deposited unmistakable crystals of phenylthiocarbamide showing that this molecule had not undergone any change.

Phenylthiocarbamide solution (50 c.c. of *N*/50) yielded 0·3352 g. of the complex containing Ag, 33·52; S, 10·08%. $PhNHCSNH_2{\cdot}AgNO_3$ requires 0·3328 g. of the complex and Ag, 33·32; S, 9·936 per cent.

Expt. 3. *Action of Potassium Thiocyanate Solution on the above Complex.*—The precipitate formed above was suspended in 50 c.c. of dilute nitric acid and treated with 15 c.c. of *N*/10-potassium thiocyanate. By filtering and titrating back, the amount of thiocyanate used up by interaction with the silver complex was determined.

TABLE II.

Time (hour) ...	¼	½	6	24
N/10-KSCN used (c.c) ...	5	6	9	9

The same product was slowly obtained by the interaction of freshly precipitated silver thiocyanate with a solution of phenylthiocarbamide. It was obtained more readily as follows.

Expt. 4. *Action of Silver Nitrate on a Mixture of Phenylthiocarbamide and Potassium Thiocyanate*—When *N*/10- solutions were mixed, the silver nitrate being added last, a precipitate was formed; the filtrate from this contained no silver and no phenylthiocarbamide; it contained only a trace of thiocyanate.

In fact it appears that the solutions of three substances, thiocarbamide, silver nitrate and thiocyanate, mixed in any order, always give the same result.

Expt. 5. *Examination of the Phenylthiocarbamide-Silver Thiocyanate Complex.*—Heated on a nickel foil it fused without evolving fumes. It was insoluble in alcohol or water. Hot water and strong nitric acid decomposed it, whilst cold dilute acid had only a very slight action.

From 50 c.c. of the thiocarbamide solution the yield of the complex was 0·3160 g. containing Ag, 34·1; S, 20·13 per cent. $PhNHCSNH_2{\cdot}AgSCN$ requires 0·3180 g. of the complex and Ag, 33·96; S, 20·01 per cent.

These results clearly explain the fact, repeatedly corroborated by titrations, that thiocyanate can be estimated by Volhard's method in the presence of phenylthiocarbamide *so long as the latter is less than equivalent to the former,* because it is precipitated with the former; whereas if the thiocarbamide is in excess, the thiocyanate cannot be estimated because thiocarbamide also interacts with silver nitrate.

It is remarkable that under conditions precisely analogous to those employed in the present investigation copper sulphate, besides forming various complexes, oxidises part of the phenylthiocarbamide to a base which on analysis and from its nitroso derivative proved to be Hector's danilino-*o*-diazothiol (*Ber.*, 1889, **22**, 1176). No evidence of any such change has been found when using silver nitrate.

SUMMARY.

1. Silver nitrate unites with phenylthiocarbamide in acid solution to form several complexes and the compound $PhNHCSNH_2{\cdot}AgNO_3$ is formed in the presence of excess of aqueous silver nitrate, 10-12% extra silver nitrate being used up in the latter case.

2. Potassium thiocyanate interacts with the above compound and changes it to phenylthiocarbamide-silverthiocyanate.

3. Thiocyanate can be conveniently estimated with a fair degree of accuracy in the presence of phenylthiocarbamide by Volhard's method under the conditions described but only if the phenylthiocarbamide is present in a quantity less than one equivalent to the thiocyanate.

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THE PHENYLTHIOCARBAMIDES. A CONTRIBUTION TO THE STUDY OF THE TRIAD -N·C·S-. PART V. ACTION OF NITROUS ACID ON αα'-METHYL-PHENYLTHIOCARBAMIDE.

By Kunj Behari Lal and Hans Krall.

Mehta and Krall (*J. Indian Chem. Soc.* 1935, **12**, 635, 640) studied the action of nitrous acid on monophenylthiocarbamide and found that two changes occurred simultaneously : (*i*) oxidation of phenylthiocarbamide to Hector's base, and (*ii*) the "normal" reaction of nitrous acid on amides with the production phenylmusturd oil and further they found that strong acids facilitated the former change, weak acids the latter.

$$\mathrm{PhNHCSNH_2} \rightarrow \mathrm{PhNHCSOH} \rightarrow \mathrm{PhNCS} + \mathrm{H_2O}.$$

The samereaction has now been extended to αα'-methylphenylthiocarbamide with the object of ascertaining the effect of the presence of a positive group.

In the presence of hydrochloric acid, an evanescent wine-red colouration is produced suggesting the transient formation of a thionitrite (Tasker and Jones, *J. Chem. Soc.*, 1909, **95**, 1917), whilst a gas consisting chiefly of NO (83 %) is rapidly evolved, the reaction mixture containing a base which yields a crystalline perchlorate and picrate and appears to be methylphenylformamidine disulphide formed thus :

$$2\mathrm{Ph(Me)NC(NH)SH} \rightarrow 2\mathrm{Ph(Me)NC(NH)S{\cdot}NO} \rightarrow$$

$$2\mathrm{NO} + [\mathrm{Ph(Me)NC(NH)S}]_2.$$

The simultaneous occurrence of a subsidiary reaction, just as in the parent compound, is shown by the evolution of nitrogen (17%) and the presence in the reaction mixture of sulphuric acid (10%), methylaniline and some solid. The base is prone to further oxidation and when larger proportions of sodium nitrite are used, an oil is produced, whilst the amount of the solid, sulphuric acid, NO and nitrogen is correspondingly increased. Traces of COS and $\mathrm{CO_2}$ are also present in the gas phase.

In the presence of acetic acid, on the other hand, sodium nitrite reacts slowly with the thiocarbamide and the gas phase is mostly nitrogen (85%) but it contains also carbon oxysulphide No formamidine disulphide is produced and the evolution of nitrogen, agreeing with the action of phenylthiocarbamide in the same conditions, suggests the normal behaviour of amides, and the product formed might be expected to decompose into

$$Ph(Me)NCSNH_2 \longrightarrow Ph(Me)NCSOH$$

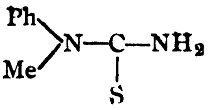
methylaniline and carbon oxysulphide. Free methylaniline is not found but the reaction mixture contains two solids and an oil of complex character, evidently resulting from the mutual interaction of the above substances. In this case the oxidation reaction is a subsidiary one, nitric oxide being produced in smaller quantity (5%). Excess of sodium nitrite brings about secondary decompositions as in the presence of hydrochloric acid.

It is clear, therefore, that nitrous acid acts on αα-methylphenylthiocarbamide according to the following equations :

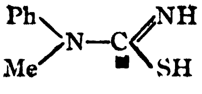
$$(i)\quad 2Ph(Me)NCSNH_2 + 2HNO_2 = Ph(Me)NC(NH)\cdot S\cdot S\cdot (NH)CN(Me)Ph + 2NO + 2H_2O$$

$$(ii)\quad Ph(Me)NCSNH_2 + HNO_2 = Ph(Me)NCSOH + N_2 + H_2O.$$

The presence of acids facilitates the former change. The evolution of nitrogen in (*ii*) is an evidence for the structure (I) which is thus the predominant tautomer in neutral solutions. Acids evidently facilitate the change of this to a form which does not contain the amino group as in (II).



(I)



(II)

It will be noticed that while phenylthiocarbamide yields a diazothiol (Hector's base) with the greatest ease by oxidation with various reagents, including nitrous acid, methylphenylthiocarbamide, which gives such a diazothiol with iodine or hydrogen peroxide (Gabriel and Hofmann, *Ber.*, 1892, **25**, 1578; Chakrabarti and De, *J. Indian Chem. Soc.*, 1928, **5**, 661) gives a formamidine disulphide with nitrous acid, thereby resembling thiocarbamide itself (Werner, *J. Chem. Soc.*, 1912, **101**, 2180). There is no evidence that the formamidine disulphides break down to diazothiols and in the light of the present investigation it appears that Hector's base, which is produced with extreme ease under these conditions from the parent compound, is a direct oxidation product of phenylthiocarbamide and that no intermediate disulphide compound need be postulated (*cf.* Fromm and Heyder, *Ber.*, 1909, **42**, 3804). The proximity of the methyl group to the phenyl nucleus in the methyl homologue seems, however, to prevent oxidation into a Hector's base the production of which is, therefore, dependent on the free α-hydrogen atom. The feeble base obtained by Dost (*Ber.*, 1906, **39**, 1014) by the action of sulphuryl chloride on the methylphenylthiocarbamide in chloroform solutions does not appear to be formed under our conditions.

EXPERIMENTAL.

All the gasometric experiments were carried out in a Lunge's nitrometer. It was found convenient to use a solution of sodium nitrite containing one mg. molecule $NaNO_2$ per c.c. The requisite amount of sodium nitrite was added by introducing definite volume of this solution with the aid of 1 c c. pipette graduated in tenths of a cubic centimetre.

Expt. 1. *Action of Nitrous Acid on αα-Methylphenylthiocarbamide in presence of* N-*Hydrochloric Acid* (*Gas phase*).—0·083 G. of thiocarbamide (½ mg.) was introduced into the nitrometer with the help of 1 c.c. of alcohol. To enable the reaction to begin in acid solution, 1 c c. of 4*N*-hydrochloric acid * was added before the addition of the nitrite solution. The cup of the nitrometer was then washed down with 0·5 c.c. of water. The above solution was then treated with 0·5 c.c. of sodium nitrite solution (½ mg.) and the cup of the nitrometer further washed with 1 c.c. of water. The reaction was brisk and invariably took place with the production of an evanescent wine-red colour. The reaction mixture becomes finally pale yellow and the evolution of the gas was complete in half an hour. Gas collected, 12·7 c.c. at 22° and 748 mm., *i.e.*, 11·3 c.c. at N. T P. and contained N, 17; NO, 83 per cent.

The gas evolved in the above experiment was expelled from the nitrometer and 0·5 c. c. of $NaNO_2$ solution (½ mg.) more added to the residual liquid in the nitrometer. 9·8 C.c. of the gas at N. T. P. were further evolved with the production of a slight red colouration and contained N, 38% ; NO, 50% ; $COS+CO_2$, 12% (determined by absorption in concentrated alkali, *cf. Expt.* 4). It was observed that upto five molecular proportions of nitrous acid could thus react to produce mainly secondary decomposition in which the proportion of the residual gas left after treatment with alkali and $FeSO_4$ solutions rose up to 40% of the total gas evolved. This residual gas was wholly nitrogen because it was unaffected by

* To avoid unnecessary dilution, acid of this strength was used.

ammoniacal cuprous chloride solution and by bromine, showing the absence of CO or unsaturated hydrocarbons

In these experiments sulphuric acid was detected in the residual liquid left behind in the nitrometer There was no evidence of the production of thiocyanic acid or free sulphur during the reaction. This experiment was next done on a large scale to study more closely other reaction products, neglecting those present in the gas phase.

Expt. 2. *Action of Nitrous Acid on αα′-Methylphenylthiocarbamide in Molecular proportions in presence of* N-*Hydrochloric Acid, neglecting the Gas Phase.*—Hydrochloric acid (4 *N*-, 100 c.c) was added to the cold solution of αα′-methylphenylthiocarbamide(8·3 g.) in 200 c.c. of 50 % warm alcohol in a 500 c c. flask. The flask was kept in a water-bath at a temperature of 19-20°. A solution of 3·5 g. of sodium nitrite (98·5% pure) in 100 c c. of water was slowly added to the thiocarbamide solution, with constant shaking during the course of an hour. The red colouration produced on the addition of the nitrite solution persisted more or less for about 25 minutes. The solution then turned pale yellow and more addition of the nitrite solution did not produce further change in colouration. After the addition of the nitrite solution the flask was put aside for an hour to complete the reaction. Small amount of solid separated which when viewed under the microscope appeared to be those produced in larger amount in presence of acetic acid (*cf. Expt.* 5). There was no separation of sulphur during the experiment. The solution was filtered from the insoluble matter and the clear filtrate examined as follows:

(*a*) 50 C c. of the solution were just neutralised with ammonia when an emulsion was formed which on stirring gave rise to a reddish-brown oil. The supernatant liquid was carefully decanted, the oil washed with a little water and extracted with ether. About 0·5 c.c. of the oil, obtained from the ethereal extract, was treated with 1 c.c. of 4*N*-hydrochloric acid when an immediate separation of sulphur took place. The acid solution was decanted off the residual oily matter. It gave Libermann's nitrosoamine reaction, suggesting the presence of methylaniline formed in the original reaction mixture. The oil decomposed by itself into sulphur and other product when it was heated at 80° or kept as such overnight. There was, however, no precipitation of any base, corresponding to Hector's base in the parent compound, on neutralisation of the acid reaction mixture.

(*b*) 200 C.c. of the original acid mixture were boiled under reflux for an hour. It shortly turned slightly pink and got turbid. The pink colour disappeared but the turbidity was latter followed by the production of a light yellow mass of sulphur (0·21 g.). The residual mother liquor from this contained thiocyanic acid, undoubtedly formed as a result of the hydrolysis of some free thiocarbamide which was in fact detected in the residues obtained by evaporating the reaction mixture to dryness. The same sequence of changes occurs in the original reaction mixture if it is kept as such for several days.

(*c*) 50 C.c. of saturated ammonium perchlorate solution were added to 50 c.c. of the acid reaction mixture when an emulsion was produced which separated as an oil the next day. When placed in a vacuum over sulphuric acid it soldified to a brittle mass. It was crystallised from methyl alcohol and ether by cooling in ice, m.p. 143° (decomp.). It contains N, S, Cl and on boiling in aqueous solution it decomposes to give products as in (*b*) above.

(*d*) 50 C.c. of 1% aqueous picric acid solution were added to 50 c.c. of the reaction mixture. An amorphous yellow mass at once separated. This was found to be due to the presence of methylaniline in the original solution. The liquid was decanted off this amorphous mass. A light yellow precipitate was formed on keeping overnight which was crystallised from methyl alcohol, m.p. 140°. It contains S and N and decomposes on boiling with water like the perchlorate. When the precipitate of the picrate was crystallised from hot ethyl alcohol, some of it seemed to decompose into sulphur and other products.

(*e*) 50 C.c. of the acid solution were treated with a solution of barium chloride. The $BaSO_4$ so obtained weighed 0·1382 g. pointing to the oxidation of about 10% sulphur to sulphuric acid. The behaviour of the acid reaction mixture thus suggested the presence of methylphenylformamidine disulphide hydrochloride in solution to which decompositions, mentioned in (*a*) and (*b*), could be attributed. Moreover, the formation of a crystalline perchlorate and a picrate from the aqueous solution confirmed the presence of this base in solution. The salts of this base with most of the commoner acids appeared to be extremely soluble or else products of indefinite oily character.

If in this experiment two or more molecular proportions of sodium nitrite were employed, the reaction was marked by the production of an oil (*vide* expt. 5), more solid and sulphuric acid.

Expt. 3. *Action of Nitrous Acid on αα′-Methylphenylthiocarbamide in presence of Acetic Acid* (*Gas phase*).—αα′-Methylphenylthiocarbamide

(0·083 g.) was introduced into the cup of the nitrometer with the aid of 1 c.c. of alcohol. To enable the reaction to begin under nearly neutral conditions 0·5 c.c. of sodium nitrite solution was added before the addition of 2 c.c. of 2*N*-acetic acid solution to the thiocarbamide in the nitrometer. The liquid got turbid at first and then gas was evolved in an hour. The residual liquid contained no thiocyanic acid and only traces of sulphuric acid. Gas evolved, 11·8 c.c. at 23° and 749 mm. *i.e.*, 10·4 c.c. at N.T.P and contained N, 85% ; NO, 5%. COS, 10%. (*cf.* Expt. 4). In this case also, more addition of nitrite solution evolved more gas in which the proportion of nitrogen was however less (48%).

In the gasometeric experiments 1 and 3 it was found that a gas was also evolved which imparted a yellowish tinge to strong solution of alkali which then gave test for sulphide In the following experiment this gas was subject to closer examination.

Expt. 4. *Examination of the Sulphurous Gas produced in Expts.* 1 *and* 3.—aa'-Methylphenylthiocarbamide (8·3 g) was dissolved in 200 c c of 50% alcohol contained in a 750 c.c. round-bottomed flask. Sodium nitrite (3·5 g.) dissolved in 100 c.c. of water was further added to the cold thiocarbamide solution. 100 C.c. of 2*N*-acetic acid were then gradually added to the above solution and the temperature was kept at 22°. The evolved gas was successively driven through three absorption flasks containing the following reagents.

(*i*) Saturated copper sulphate solution acidified with its own volume of concentrated sulphuric acid (50 c.c.).

(*ii*) 33% Aqueous caustic potash solution (50 c.c.).

(*iii*) Alcoholic caustic potash solution (30 c.c.).

No precipitate of CuS was formed in (*i*), whilst (*ii*) had a yellowish tinge which later disappeared. The alkaline solution in (*ii*) gave a feeble test for sulphide. The alcoholic solution in (*iii*), however, gave no test with sodium nitroprusside or lead acetate in the cold but on boiling the solution, lead acetate gave a copious precipitate of lead sulphide. Also the alcoholic solution did not give any precipitate with dilute copper sulphate solution, showing the absence of carbon disulphide in the gas. These observations show that the gas is COS.

In this experiment it was observed that the reaction flask contained some brown oily mass adhering to a solid. The solid was freed from the oil by digesting with alcohol, yield 2·8 g. In another experiment it was found that the amount of the oil was greater when larger proportions of nitrous acid were used, whilst the amount of the solid was not greatly affected (3 g.). In the next experiment the solid and the oil were investigated.

Expt. 5. *Examination of the Products of the Reaction formed in presence of Acetic Acid, Neglecting the Gas Phase.*—The solid isolated in the above experiment was found to be a mixture of two compounds which are hard to separate by means of the common organic solvents. A chloroform-alcoholic solution of these solids, however, deposited the more insoluble constituent in blocks The latter compound softend at 192° and melted at 199° (decomp). [Found : N, 7·59, 7·55; S 34·44, 34·6 ; M.W. (Rast's method), 380]. It was not acted upon by dilute acid and alkali but was slowly attacked by concentrated acid and alkali on prolonged boiling. In the decomposition with alkali some sulphide was detected in the decomposition products but in neither case free methylaniline could be detected in the products of the reaction, though there was evidence of the presence of a secondary amino group. An alcoholic suspension of 0·3196 g. of the solid when boiled for 4 hours with ammoniacal silver nitrate gave 0·8830 g. of Ag_2S showing that all of the sulphur in the compound could thus be removed by this reagent. (Theory required Ag_2S, 0·8421 g.). Mercuric oxide was less effective for this purpose. In both these cases the alcoholic solution obtained after desulphurisation was coloured violet which gave a water-soluble residue on evaporation to dryness. Alkaline lead acetate remained unaffected when so treated with the solid. These properties and the analytical results rather point to the probable molecular formula of this compound to be $[C_6H_4N(Me)CS_2]_2O$.

The more soluble compound (m p. 205°-10°) was obtained from the chloroform-alcoholic mother liquors in fine needles. It was still contaminated with a small amount of the above compound which could not be removed even after repeated crystallisations from toluene. It contained nitrogen (10%) and sulphur (23%). It resembled in most of its properties with the previous compound but differed from the latter in that it gave thiocyanic acid with alcoholic ammonia. The oil usually obtained in these experiments (*cf Expts.* 2 and 4) was found to distil at 230° and was volatile in steam. It was not soluble in acids and alkalis and gave thiocyanic acid with alcoholic ammonia. The aqueous mother liquor that remained in experiment 4 did not contain free methylaniline.

The action of nitrous acid on the *sym*-methylphenylthiocarbamide is in progress.

SUMMARY.

1. Nitrous acid reacts with αα-methylphenylthiocarbamide in strongly acid solution to produce mainly an oxidation change to methylphenylformamidine disulphide.

2. In the presence of weak acids the principal reaction results in the evolution of nitrogen.

3. These results are best explained by assuming that methylphenylthiocarbamide exists in neutral solution mainly as $Ph(Me)NCSNH_2$, whilst the presence of acids causes the imino tautomer $Ph(Me)NC(SH)NH$ to predominate.

4. No diazothiol, corresponding to Hector's base in the case of the parent compound, is formed under the conditions of our experiments.

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DIHYDROKURCHINE.

By J. C. Chowdhury and D. H. Peacock.

Kurchine was isolated from the bark of *Halarrhaena antidysenterica* by Ghosh and Ghosh (*J. Indian Chem Soc.*, 1928, **5**, 477). In the course of an examination of the bark of this tree (Peacock and Chowdhury, *J. Chem. Soc.*, 1935, 734) we isolated kurchine and several other alkaloids. We tried to reduce these in ethyl alcohol solution by Adams, platinum oxide method; with conessine (Haines, *Pharm. J.*, 1865, *ii*, **6**, 432) lettocine (Peacock and Chowdhury, *loc. cit.*), *iso*conessimine (Siddiqui, *J Indian Chem. Soc.*, 1934, **11**, 283) and conimine (Siddiqui, *loc. cit.*); no reduction was observed Kurchine ($C_{23}H_{38}N_2$) gave dihydrokurchine ($C_{23}H_{40}N_2$) as an oil which could not be obtained crystalline. Dihydrokurchine gave a dihydriodide ($C_{23}H_{40}N_2$, 2HI), m.p. 212°, a neutral sulphate ($C_{23}H_{40}N_2,H_2SO_4$), very sparingly soluble in water, m.p. 334° and a picrate, m.p. 176°. Kurchine itself was not acetylated by heating with acetic anhydride but dihydrokurchine gave an acetyl compound [$C_{23}H_{39}N_2\cdot(COCH_3)$], m.p. 112°. It would appear, therefore, that of the two tertiary nitrogen atoms in kurchine one is combined as $:>C:N-$ and on reduction gives $>CH\cdot NH-$. Dihydrokurchine gave a nitroso derivative ($C_{23}H_{39}N_2\cdot NO$), m.p. 109°, and a *p*-toluenesulphonyl derivative ($C_{23}H_{39}N_2\cdot SO_2C_6H_4Me$), m.p. 174°. Dihydrokurchine is thus a secondary base.

EXPERIMENTAL.

Dihydrokurchine.—Kurchine (1·3 g.) was mixed with platinum oxide (0·05 g.) and rectified spirit (36 c.c.) and shaken in an atmosphere of hydrogen for 1½ hours at 28-30°. Reduction then appeared complete, the volume of hydrogen absorbed was 135 c.c. corresponding approximately to the addition of one molecule. The solution was filtered from platinum, acidified with hydrochloric acid and the ethyl alcohol removed under reduced pressure. The residue was dissolved in water and a solution of sodium sulphate added, when the sparingly soluble dihydrokurchine sulphate was precipitated. It was recrystallised from rectified spirit in colourless needles, m.p. 334 (decomp.). (Found: SO_4, 21·1, 21·7. $C_{23}H_{42}O_4N_2S$ requires SO_4, 21·7 per cent). The base liberated from the sulphate was a colourless oil soluble in acetone, ether, petrol ether, benzene and chloroform.

Dihydrokurchine Hydriodide.—It was precipitated as an oil by adding a strong solution of potassium iodide to a solution of the hydrochloride of the base. It crystallised from hot water as colourless prisms, m.p. 222°, sparingly soluble in cold water, readily soluble in methyl and ethyl alcohol. (Found: I, 42·07, 42·1. $C_{23}H_{42}N_2I_2$ requires I, 42·3 per cent). *Dihydrokurchine picrate* crystallised from ethyl alcohol, m.p. 176°.

When lettocine, conessine, *iso*conessimine and conimine were similarly treated no reduction was observed.

Acetyldihydrokurchine.—Dihydrokurchine (0·2 g.) was mixed with anhydrous sodium acetate (0·5 g.) and acetic anhydride (5 c.c.) and heated for 3 hours on an oil-bath at 135-140°. The acetic anhydride was removed under reduced pressure and the residue dissolved in water, basified with ammonia and extracted with ether. The ether was removed when an oil was obtained which is readily soluble in acetone, methyl alcohol, ethyl acetate and benzene; sparingly soluble in petrol ether. It was dissolved in methyl alcohol and neutralised with dilute sulphuric acid. The acetyl dihydrokurchine sulphate crystallised on cooling as colourless needles from hot water, m.p. 268°. [Found: SO_4, 10·03, 10·01. $(C_{25}H_{42}ON_2)_2$, H_2SO_4 requires SO_4, 11·0 per cent]. The base, liberated from the sulphate by caustic soda, was taken up in ether, the ether removed and the residue repeatedly crystallised from rectified spirit when it was obtained as colourless needles, m.p. 112°.

Kurchine similarly treated was not acetylated.

Nitrosodihydrokurchine.—Dihydrokurchine (0·8 g.) was dissolved in 10% acetic acid (15 c.c.), cooled and a solution of sodium nitrite (0·5 g.) in water (5 c.c.) slowly added. The nitroso compound which separated was filtered, washed with water and repeatedly crystallised from rectified spirit. *Nitrosodihydrokurchine* separated as pale yellow crystals, m.p. 100°, sparingly soluble in ether, petrol ether and ethyl acetate; soluble in acetone, acetic acid and ethyl alcohol. (Found: N, 11·0. $C_{23}H_{39}ON_3$ requires N, 11·26 per cent).

p-*Toluenesulphonyldihydrokurchine.*—Dihydrokurchine (0·8 g.) was mixed with 10% caustic soda solution (10 c.c.) and finely powdered *p*-toluenesulphonyl chloride (10 g.) slowly added with good shaking. After 2 hours the mixture was heated to 80° to decompose unchanged sulphonyl chloride, filtered and washed. The oily crude product was repeatedly precipitated from rectified spirit and finally obtained crystalline. p-*Toluenesulphonyldihydrokurchine* is readily soluble in acetone, ethyl acetate and chloroform, sparingly soluble in ether and petrol ether, m.p. 174°. (Found: S, 6·23. $C_{30}H_{46}O_2N_2S$ requires S, 6·43 per cent).

One of us (J. C. C.) wishes to thank the University of Rangoon for the award of a scholarship in order to carry out this work. We have to thank Mr. M. N. Gallant, Forest Economist, Burma and the Burma Forestry Department for the supply of the bark used in this work and the University of Rangoon for a grant in aid.

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NATURAL GLUCOSIDES. PART I. THE CONSTITUTION OF THE GLUCOSIDE PRESENT IN *MURRAYA EXOTICA*.

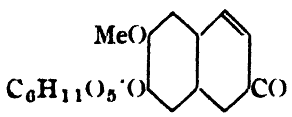
By Prafulla Kumar Bose and (Miss) Asima Mookerjee.

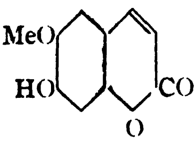
From the flowers of of *Murraya exotica*, Linn. (N. O. *Rutaceae*) de Vry and Blas (*Z. Chem.*, 1869, 310; van Rijn, "Die Glykoside,' 1931, p. 256) isolated a bitter, crystalline glucoside which was called murrayin. According to these investigators it has the molecular formula, $C_{18}H_{22}O_{10}, \frac{1}{2}H_2O$, and a melting point of 170°. It was found to dissolve in alkali with a yellow colour and a greenish-blue fluorescence. The hydrolysis of murrayin by dilute sulphuric acid afforded murrayetin according to the equation:

$$C_{18}H_{22}O_{10} + H_2O = \underset{\text{(Murrayetin).}}{C_{12}H_{12}O_5} + \underset{\text{(Glucose).}}{C_6H_{12}O_6}$$

Murrayetin, which formed small rhombic needles, m.p. 110°, dissolved in aqueous alkali with a blue fluorescence and formed a yellow lead salt.

From the air-dried petals of *M. exotica* we have been able to isolate a white crystalline glucoside in an yield of 1·3%. It melts at 218°, has a bitter taste and dissolves in alkali forming a yellow solution, which, unlike murrayin, does not show any greenish-blue fluorescence. This glucoside was found to contain 8·55% methoxy group. Hydrolysis with dilute sulphuric acid gave a crystalline aglucone which melts at 202-4°. It dissolves in alkali with an intense blue fluorescence, but unlike murrayetin does not give a yellow precipitate with lead acetate. The aglucone contained 16·17% methoxy groups. We thought that the aglucone might be identical with scopoletin (II), in asmuch as the analysis, colour reactions and the melting point of our aglucone agreed well with those of scopoletin. To confirm the identity of the two compounds, we methylated our aglucone and obtained a white crystalline methyl derivative, m.p. 142°, which was insoluble in alkali. When mixed with a synthetic specimen of esculetin dimethylether (III), which melted at 141°-2°, there was no depression in melting point. It, therefore, follows that the glucoside isolated by us from the flowers of *M. exotica* is nothing but scopolin (I), the m.p. of which is reported to be 215-17°. We believe that de Vry and Blas had an impure specimen of scopolin in their hands and this they called murrayin.





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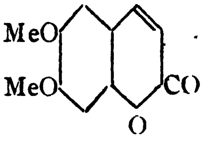

(III)

EXPERIMENTAL.

Isolation of Scopolin.—Air-dried petals (150 g.) of *M. exotica*, which were collected from the suburbs of Calcutta in June, were refluxed with 1·1 litres of rectified spirit for two hours and filtered hot. The extraction was repeated thrice with the same volume of alcohol. The combined filtrates were concentrated under reduced pressure to about 400 c.c. and treated, while still hot, with a saturated aqueous solution of lead acetate till there was no further precipitate. The yellow lead salt was filtered off and washed with hot alcohol. The lead salt was suspended in hot alcohol (300 c.c.) and saturated with sulphuretted hydrogen and the lead sulphide filtered off. The orange filtrate on concentration did not give any crystalline residue.

The filtrate, left after the removal of the lead salt, was freed from lead by means of sulphuretted hydrogen and the clear yellow filtrate was distilled under reduced pressure to remove alcohol. The residue was taken up with 100 c.c. of hot water and repeatedly shaken with chloroform (15 c.c. were used each time). During extraction with chloroform, a light brown voluminous precipitate separated out which was collected. The aqueous filtrate gave a further quantity of the precipitate on concentration on the water-bath and cooling. The combined precipitates were thrice crystallised from methyl alcohol (charcoal) when colourless needles, m.p. 218°, were obtained; yield 1·96 g. It is easily soluble in hot water and aqueous alkali, but insoluble in chloroform. (Found in material dried at 110° in *vacuo*. OMe, 8·55. $C_{16}H_{18}O_9$ requires OMe, 8·76 per cent).

Hydrolysis of the Glucoside: Formation of (II).—The glucoside (0·358 g.) dissolved in water (20 c.c.) was heated with 2 drops of concentrated sulphuric acid for 4 hours at 100°. The solution was then extracted eight times with chloroform, 10 c.c. being used each time. The combined extracts were dried over anhydrous sodium sulphate and the solvent removed on the water-bath. The brownish crystalline residue was distilled in high vacuum and then crystallised from acetone, when almost colourless needles, m.p. 202-4°, were obtained; yield 0·13 g. (Found: OMe, 16·17. $C_{10}H_8O_4$ requires OMe, 16·15 per cent).

Methylation of (II): *Formation of Esculetin Dimethylether.*—0·05 G. of (II) was mixed with 0·042 g. of methyl iodide, 5 c.c. of acetone and 0·1 g. of anhydrous potassium carbonate and the mixture was refluxed for 6 hours on the water-bath. It was then filtered and the filtrate evaporated to dryness. The residue was washed with cold water, dried and distilled in high vacuum. The distillate was finally crystallised from methyl alcohol when colourless needles, m p. 142°, were obtained. Esculetin was methylated in a similar manner using the calculated quantity of methyl iodide and the dimethylether, m.p. 141-2°, did not depress the m. p. of the above compound.

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NEW COMPOUNDS OF GALLIUM. PART II.

By Panchanan Neogi and Sarajit Kumar Nandi.

In continuation of our work (Neogi and Nandi, *J. Indian Chem. Soc.*, 1936, **13**, 399) we have succeeded in preparing some of the common inorganic compounds of the rare element gallium which have hitherto been unknown. The orthophosphate of gallium has been obtained by two different methods, *viz.*, (*i*) dissolution of the hydroxide in orthophosphoric acid, and (*ii*) precipitated by the action of sodium hydrogen phosphate on the nitrate solution. Gallium salts of hydracids of the halogens are known, but those of oxyacids of the halogens are not known. We have been able to prepare the chlorate, iodate and the bromate in solution only, which decomposes on concentration even in vacuum evolving bromine.

As regards analysis in the case of the phosphate, the salt was first dissolved in dilute nitric acid and the phosphoric acid precipitated as ammonium phosphomolybdate. In order to determine the metal, the filtrate was evaporated to a syrupy consistency with sulphuric acid, and carefully heated over a free flame until nitric acid was expelled. The residue was moistened with hydrochloric acid, taken up with water, and the molybdenum was separated as sulphide. The metal was then precipitated from the filtrate as hydroxide by means of ammonium chloride and ammonia, which was ultimately ignited and weighed as oxide.

To analyse gallium chlorate, iodate and the basic iodate, the first one was dissolved in water and the others in dilute hydrochloric acid and the gallium was precipitated as hydroxide from the solution and weighed as oxide. To estimate the chlorine in the chlorate, the filtrate from the hydroxide was first reduced to the chloride by means of ferrous sulphate and then precipitated as silver chloride. To estimate the iodine, the original iodate solution (in dilute sulphuric acid in the case of iodate and dilute hydrochloric acid in the case of basic iodate) was run into a solution of potassium.iodide containing hydrochloric acid and the liberated iodine was at once titrated with thiosulphate solution in the cold.

All the analyses were performed with the weights of substances made constant at room temperature by keeping them in air for a fairly long time.

EXPERIMENTAL.

Gallium Orthophosphate, $GaPO_4$, $3H_2O$.

This salt was obtained by just dissolving freshly precipitated gallium hydroxide in dilute solution of orthophosphoric acid. The solution was left in a vacuum desiccator for crystallisation but the solid thus obtained was insoluble in water. It was repeatedly washed with alcohol to free it from adhering phosphoric acid and again dried. The solid is also obtained by the addition of absolute alcohol to the solution. It is a white microcrystalline substance, insoluble in water, alcohol and ether, but soluble in dilute hydrochloric acid. (Found: Ga, 31·74; P_2O_5, 32·07. $GaPO_4, 3H_2O$ requires Ga, 31·96; P_2O_5, 32·42 per cent).

The same compound with identical properties was obtained as a precipitate when sodium hydrogen phosphate solution was added to a solution of gallium nitrate. The precipitate was washed with water, dried in a vacuum desiccator and then on analysis gave exactly the same composition. (Found: Ga, 32·47; P_2O_5, 32·80. $GaPO_4, 3H_2O$ requires Ga, 31·96; P_2O_5, 32·42 per cent).

Gallium Chlorate, $Ga(ClO_3)_3, H_2O$.

It was prepared by the double decomposition of the solution of gallium sulphate and barium chlorate until all barium were precipitated as sulphate. The filtrate was kept in a desiccator when needle-shaped white crystals appeared. The substance was washed with alcohol, recrystallised and dried. The salt is a white needle-shaped crystalline substance, soluble in water and hydrochloric acid, but insoluble in ether and alcohol. The salt is converted into chloride on heating. [Found: Ga, 20·43; Cl, 31·0. $Ga(ClO_3)_3, H_2O$ requires Ga, 20·67; Cl, 31·47 per cent].

Gallium Iodate, $Ga(IO_3)_3, 2H_2O$.

Metallic gallium was dissolved in nitric acid and the theoretical amount of iodic acid added to the solution; the nitric acid was driven off by evaporation on the water-bath, when white crystals of gallium iodate appeared, which was subsequently washed with water and carefully dried in a desiccator over calcium chloride. This substance is sparingly soluble in water, insoluble in alcohol and ether, but soluble in dilute hydrochloric, sulphuric and nitric acids. The salt was decomposed by concentrated hydrochloric acid with the evolution of chlorine and iodine vapours evolved on prolonged boiling with concentrated hydrochloric acid. [Found: Ga, 11·06; I, 60·84. $Ga(IO_3)_3, 2H_2O$, requires Ga, 11·09; I, 60·38 per cent].

Basic Gallium Iodate, $Ga(IO_3)_3$, Ga_2O_3, $3H_2O$.

This basic compound was obtained as a white precipitate when sodium iodate solution was added to a solution of gallium nitrate. The precipitate was washed several times with water and dried. The substance is insoluble in water, alcohol and ether, but soluble in dilute hydrochloric acid. [Found: Ga, 24·83 ; I, 45·26. $Ga(IO_3)_3$, Ga_2O_3, 3 H_2O requires Ga, 25·09; I, 45·51 per cent).

Gallium Bromate.

Gallium bromate was prepared in the same way as the chlorate, barium bromate being used in place of the chlorate. The resultant solution of gallium bromate, which was a weak one owing to the limited solubility of barium bromate, on being concentrated decomposed and bromine vapour was evolved. Hence it shows that galiium bromate is an unstable compound. Attempts were made to precipitate the gallium bromate by means of absolute alcohol, acetone, as well as alcohol and ether, but no solid bromate separated. The partly dried, salt still contained small quantities of the bromate but when the solid was completely dried there was no trace of bromine in it, and the hydrate remained.

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PHOTOCHEMICAL REACTIONS WITH SOME INORGANIC COLLOIDS AS ACTIVE AGENTS UNDER THE INFLUENCE OF LIGHT IN VARIOUS STATES OF POLARISATION

PART I TUNGSTIC ACID, MOLYBDIC ACID, CHROMIC TUNGSTATE, ETC. AS PHOTO ACTIVE REAGENTS, OPTICAL PROPERTIES OF THESE SOLS: CIRCULAR DICHROISM IN THE ULTRAVIOLET.

By J. C. Ghosh, T Banerjee and S. K Mukherji

INTRODUCTION

The most important photochemical synthesis in nature, the assimilation of carbon dioxide, takes place on the surface of the chloroplasts. Studies on the mechanism of photochemical reactions in heterogeneous systems, other than those involved in the processes, have been meagre Such studies have an additional interest in that they may throw light on the process of asymmetric synthesis. The well known experiments of Weigert and Zocher on the anisotropy of thin layers of silver halide, irradiated with polarised light, promise interesting developments (Zocher and Coper, *Z. physikal. Chem.*, 1928, **132**, 303, 313 ; Weigert, *Naturwiss.*, 1928, **16**, 163 ; *Z. physikal. Chem.*, 1929, **3B**, 377, 389; 1929, **4B**, 83).

Weigert discovered that a layer of photochloride on development after exposure to linearly polarised light has a weaker absorption for light with a direction of vibration parallel to that of the exciting beam, than for that with perpendicular vibrations (Weigert Effect, *Ann. Physik*, 1920, *iv*, **36**, 681).

Analogous to this phenomenon, Zocher and Coper discovered that the illumination of silver chloride with circularly polarised light gave a layer of silver which showed simultaneously circular dichroism and circular double refraction. Cotton showed as early as 1893 that in the case of true solution of optically active substances, circular dichroism will be observed in the neighbourhood of an absorption band which is due to an electronic system that contributes to the optical rotation (Cotton effect). This discovery was followed up with remarkable ingenuity by Kuhn and co-workers, who were able to obtain optically active products by photochemical decomposition of solutions of ethyl α-bromopropionate and α-azide-propionic dimethylamide with circularly polarised light (*Z. physikal. Chem.*, 1930, **7 B**, 292 ; *Naturwiss.*, 1929, **17**, 227 ; 1930, **18**, 183).

It is not unreasonable to expect that photochemical reactions taking place on photo-active surface of micelles, where the molecules are arranged n a definite pattern, will show many peculiarities which are not observed in homogeneous photochemical reactions. The nature of these patterns and consequently the optical and surface properties of these micelles may undergo considerable variation if, during the aggregations of the constituent molecules to form the micelles, they are exposed to different types of polarised beams of light which they are capable of absorbing. It is because of this expectation that in our experiments, the reagents responsible for sol formation were in most cases exposed to radiations of different types, immediately after they are mixed together and attempts at purification from electrolytes by dialysis and other processes were avoided. Many sols are known where the micelles have been found to be needle-shaped or disc-shaped and have microcrystalline structure. It is probable that these sols, rather than those where the particles have amorphous structure and spherical shapes, will have stable characteristic orientation of the molecules during micelle formation and exhibit optical anisotropy. Our experimental results which are recorded in the following papers indicate unmistakably that in many cases circular dichroism in photo-active sol can be detected and in all such cases, a differential effect can be observed in the velocity of photochemical reactions when exposed to the same intensity of oppositely circularly polarised light.

Following up his pioneering work on micro-heterogeneous catalysis, Bredig and collaborators have demostrated the parallelism between selective enzyme action and that of simple optically active catalysts. Bredig and Fiske found that the addition of hydrocyanic acid to benzaldehyde in presence of (+) quinine or (−) quinidine, followed by hydrolysis resulted in the formation of (+) or (−) mandelic acid respectively (*Biochem. Z.*, 1912, **46**, 7). Bredig and Gerstner have found that dimethylamino groupings introduced into the structure of cotton fibre gave a catalyst which led to the formation of *l*-rotatory mandelonitrile (*Biochem. Z.*, 1932, **250**, 414).

We believe that we have in our experiments been able to prepare by illumination with circularly polarised light micro-heterogeneous systems having asymmetric photo-active properties.

Vanadic Acid Sols.

It is well known that vanadium pentoxide is photosensitive ; it becomes black when exposed to light in contact with glycerol, benzaldehyde, etc.

When solutions of citric acid or tartaric acid are illuminated in presence of vanadium pentoxide, bluish green solutions are obtained (Renz, *Helv. Chim. Acta,* 1921, **4**, 961). A thorough quantitative study of the mechanism of these reactions using monochromatic radiations and vanadic acid sol has not been made. This sol has got many peculiar properties. Freundlich and Leonhardt observed the phenomenon of streaming double refraction (*Koll.-Chem. Beih.*, 1915, **7**, 172). According to Reinders this birefringence is not observed with freshly prepared colloidal solutions of vanadium pentoxide. On keeping, the double refraction is developed due to the formation of needle-shaped microcrystalline micelles (*Proc. Akad. Amsterdam,* 1916, **19**, 189). Kruyt studied the Tyndall-effect of these sols in an electric field. This effect becomes very pronounced when the field is perpendicular to the luminous beams (*Verls. Akad. Amsterdam,* 1918, **18**, 1625). Wiegner (*et al*) has given a concise and clear resumé of these properties (*Kolloid Z* , 1922, **30**, 145). Errera found that a sol, five years old containing 14 parts of vanadium pentoxide per thousand, had a specific inductive capacity of 400 (*Kolloid Z.*, 1922, **31**, 59 ; 1923, **32**, 157, 372). Lange studied the polarisation of the Tyndall light from the sol and concluded that the particles were not spherical in shape (*Z. physikal. Chem.*, 1928, **132**, 21). Zocher (*et al*) have studied the thixotropic properties of the sol and noticed that these sols within certain range of concentrations separate into two phases, one isotropic and dilute, the other anisotropic and concentrated (*Kolloid Z.*, 1927, **41**, 220). He has also described the various methods for determining the anisotropy of colloidal particles (*Kolloid Z.*, 1925, **37**, 347).

The application of " Azimuthblende " to dark ground illumination enabled Szegvari to study the regional orientation of needle-shaped micelles, and he concludes that " Die fast ausschliesslich nadelförmigen Teilchen des Vanadium pentoxide soles sind gebietweise Untereinander parallel orientiert" ...."Die dauernde Doppelbrechnung, die diese sole in makroscopischen Schichten zeigen ist auch verstandlich.... .Eine so einmal erzeugte makroscopische Orienterung der an sich microskopisch orientierten Gebiete wird nach Aufhoren des sie verursachenden Geschwindigkeitsgefalles bestehen bleiben" (*Z. physikal. Chem.*, 1924, **112**, 300, 304).

Tungstic Acid Sols.

Wasiliewa observed that when a colloidal solution of tungstic acid is illuminated in presence of dextroses, formaldehyde, etc., a blue solution due to reduced tungstic acid is obtained (*Z. Wiss. Phot.*, 1913, **12**, 1 ; *cf.*, also Ghosh and co-workers, *J. Indian Chem. Soc.*, 1929, **6**, 231, 975). Ghosh and Bhattacharyya have studied the effect of ageing of sols of tungstic acid and molybdic acid on their capacity for the photoreduction of ethyl alcohol (*J. Indian Chem Soc.*, 1930, **7**, 720)

It was observed long ago by Graham that when a dilute solution of hydrochloric acid is added to a solution of sodium tungstate until the liquid becomes acid, a colloidal solution of tungstic acid is formed. Huttig and Kurre (*Z. anorg Chem.*, 1922, **122**, 44) from a study of dehydration curves deduced that yellow tungstic acid prepared from a boiling solution is a compound H_2WO_4, but that the white product prepared in the cold is a colloid behaving as a conglomerate of tungsten trioxide particles arranged in an irregular manner Jander and Winkel (*Z. physikal. Chem.*, 1930, **149**, 97) found that the normal tungstate exists in solution between p_H 6·5 and 14 ; between p_H 1·5 and 5, tungstic acid exists in polymerised colloidal form.

The shape of the micelles of tungstic acid have not been fully studied. Wiegner states that they are flat and disc shaped (*J. Soc. Chem. Ind.*, 1931, **50**, 110 T)

Dumanski und Djatschkowski (*Kolloid Z*, 1929, **48**, 49) conclude "Die allmähliche Komplexation von weinsauren Komplexen durch Eintritt von WO_3 Radikalen fuhrt zunachst zu grobdispersen Kolloiden, bei weiterer Sattigung aber zu hochdispersen Kolloid-systemen. Die untersuchten Kolloid-systeme, besitzen thixotrope Eigenschaften und die Gele besitzen such photo-chemische Empfindlichkeit." Freundlich and Kross (*Kolloid Z.*, 1930, **52**, 40) in their studies on titanium dioxide sols observe that these sols are thixotropic but ultramicroscopic investigation does not reveal any deviation from spherical shape. The strong depolarisation of the Tyndall light is, however, in agreement with the general expectation that concentrated thixotropic sols should exhibit positive streaming double refraction. Tungstic acid sols, which also exhibit thixotropy may, therefore, be expected to possess optical anisotropy.

Molybdic Acid Sol.

Graham obtained a colloidal solution of molybdic acid by the addition of hydrochloric acid to a solution of sodium molybdate. According to Britton and German who carried out electrometric titration of solutions of sodium molybdate with hydrochloric acid, an inflexion point is observed at p_H 4·8, below which a highly ionised polymolybdic acid exists (*J. Chem. Soc.*, 1930, 2154).

$$H_2[O(MoO_3)_x] \rightleftharpoons 2H^+ + [O(MoO_3)_x]''$$ where x is about 4.

Dumanski and co-workers studied the conductivity and freezing point lowering of solutions obtained by adding acids to sodium molybdate. The colloidal molybdic acid was not coagulated either by cooling or heating and had a mol. wt. of the order of 1200 (*Kolloid Z.*,1926, **38**, 208). Wohler and Engels conclude that depending on conditions of experiment, molybdic acid can be obtained in the colloidal state. On acidifying, the molybdic acid polymerises, but the particles are so small that the solution on prolonged dialysis diffuses through a parchment (*Koll.-Chem. Beih.*, 1910, **1**, 454). Ghosh and Bhattacharyya have studied the photochemical reduction of colloidal molybdic acid by ethyl alcohol (*J. Indian Chem. Soc.*, 1930, **7**, 717).

The authors are not aware of any investigation which had for its objects the determination of the shape of the particles of molybdic acid sol.

S. Ghosh and N. R. Dhar (*Z. anorg. Chem.*, 1929, **184**, 135 ; 1930, **190**, 425) observe " dass frisch aus Ammoniummolybdat und Salzsäure hergestelltes Sol von Molybdänsäure grosse Mengen Molybdansaure molekular gelost enthalt, welche sich allmahlich zu grosseren Molekeln und Kolloidteilchen vereinigen und schliesslich ausgefallt werden, wenn die zusammenballung fortschreitet."

Uranic Acid Sol.

Diachkovoski (*British Chemical Abstracts*, 1927, 1137), has studied the properties of uranic acid sols. The velocity in electric field corresponds with a negative charge of $1·984 \times 10^{-8}$ E.S.U.

Aloy and Valdignie (*Compt. rend.*, 1923, **176**, 1229) observed that if a mixture of uranium salt, dextrose and methylene blue in solution is exposed to light, the dextrose is oxidised and methylene blue reduced, the uranium playing the rôle of photocatalyst.

Chromium Hydroxide Sol.

A very large number of investigations have been carried out with chromium hydroxide sol, since it was first obtained by Graham by peptising the freshly precipitated oxide with chromic chloride and subsequent dialysis. A positive hydrosol is obtained in this way. On the other hand the green sol obtained by adding excess of alkali to a solution of chromic salt is negative. The structure of the micelles has been studied by Wintgen and Lowenthal, Wintgen and Kuhn (*Z. physikal. Chem.*, 1929, **109**, 391 ; 1928, **138**, 149). who found that the following equation holds good,

$$\text{Log } A_L = -0{\cdot}707 \log \frac{[\text{Cl}]}{[\text{Cr}]} + 44$$

where A_L is equivalent aggregation

Chromium Tungstate Sol. Our knowledge of this sol is meagre. Its method of preparation has been described in a paper by Banerjee (*J. Indian Chem. Soc.*, 1937, **14**, 59).

B. General Experimental Arrangement for the Study of Photochemical Reactions in Polarised Light.

The experimental arrangement is described in Fig. 1. The source of light was a point source quartz mercury lamp which was run from a battery of 30 volts. An ammeter in circuit and a variable external resistance were used to keep the strength of current constant at value between 2 and 2·6 amperes.

The following filters were used for isolating monochromatic radiations:—

For $313\mu\mu$, $334\mu\mu$ } Chance Bros. ultraviolet filter (1 cm.).

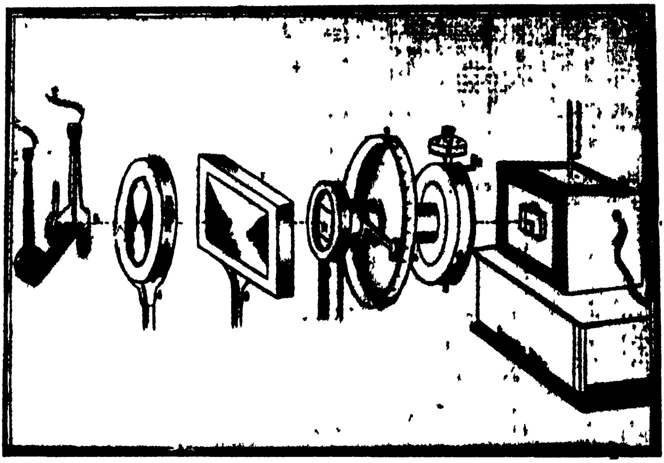
$366\mu\mu$—Schott and Gen ultraviolet filter no. 312.

$436\mu\mu$, $579\mu\mu$ } Zeiss monochromats.

In the case of red light, a thousand c.p. point-o-lite Ediswan lamp was used with suitable filters.

Light from the lamp was rendered parallel by a quartz lens placed at its focal distance from the lamp and passed into the reaction vessel kept inside a double jacketted box through a window of fused quartz plate. The temperature was kept constant within 0·1° by circulating water from a thermostat through the annular space of the box. The reaction vessel was a rectangular stoppered cell made of plane parallel plates of fused transparent silica. No cement was used, the rectangular joints being fused to one another. The closed stopper which was very well ground into a circular aperture in the thick top-plate of the reaction cell was in some cases replaced by a hollow stopper with inlet and exit tubes for bubbling pure nitrogen. The intensity of incident radiation was varied by using quartz lenses of different focal lengths. The method of measuring intensities actually absorbed by the reaction mixture consisted in first observing the deflection in a Moll galvanometer with a Moll surface thermopile covered with a quartz window and placed immediately behind the reaction cell which contained only water. The deflection was next noted when the cell was filled with the reacting mixture. The difference gave the quantity of radiant energy absorbed by the reacting system. The thermopile recording system was frequently calibrated by means of a standard incandescent lamp tested by the National Bureau of Standards, Washington. The scattering power for light was found to be very small in the case of the sols, which we have studied (*vide* Part VIII*).

FIG 1.



Description and the Working Principle of the Polarising Apparatus especially Constructed for the Purpose.

Plane polarised light was obtained by interposing in the path of the parallel beam a prism (N) of the Glans type supplied by Bernard Halle.

This was fitted with a graduated circle (G) and the rotation of the prism can be read from a vernier (Z) attached to the stand.

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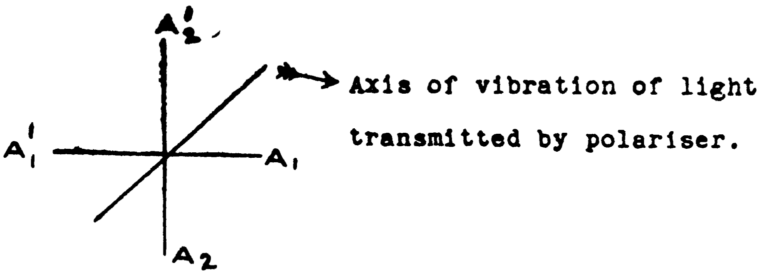
* To be published in the next issue of this Journal.

The circularly polarised light was obtained with the help of the polarising prism and a quartz quarter wave plate (Q), specially constructed for the purpose by Carl Zeiss. The latter was of the type for which the path of retardation between two principal components can be adjusted to the exactly λ 4 for any given wave-length by means of a calibrated rotating drum (D), (R is the pointer which reads the wave-length on the drum), which slides the component parts of the quartz combinations with respect to each other. The direction of vibration of light transmitted by the polarising prism was determined by reflecting it at very near Brewsterian angle from a plane glass plate.

The axis of retardation of the $\lambda/4$ combination was determined by combining it with a Fresnel's Rhomb so that the principal directions of the former may be in the plane of incidence for the latter, and perpendicular to it respectively. When introduced between crossed nicols, if they restore the light strongly, the axis of retardation for the $\lambda/4$ plate is the same as for the Fresnel's Rhomb. Otherwise, they are at right angles to each other.

A_1 A'_1, A_2, A'_2 are the principal axes of the $\lambda/4$ plate. Let light be incident from below in the plane of the paper, when A_2 A'_2 is the axis of retardation, the rotation is anticlockwise or *dextro*-rotatory and corresponds to right handed circular polarisation or *d*-circular polarisation. On the other hand, A_1 A'_1 is the axis of retardation, the emerged light is left-handed circularly or *l*-circularly polarised light (*vide* fig. 2.)

Fig 2.



C. Measurement of Circular Dichroism.

Kuhn and Braun (*Z. physikal. Chem.*, 1930, **8B**, 446) have developed a method for the determination of circular dichroism in the ultraviolet based on the principle that the axial relations of an elliptically polarised beam of light are changed on passing through a medium which has different absorption coefficients for *d*- and *l*-circularly polarised light. "Durch eine

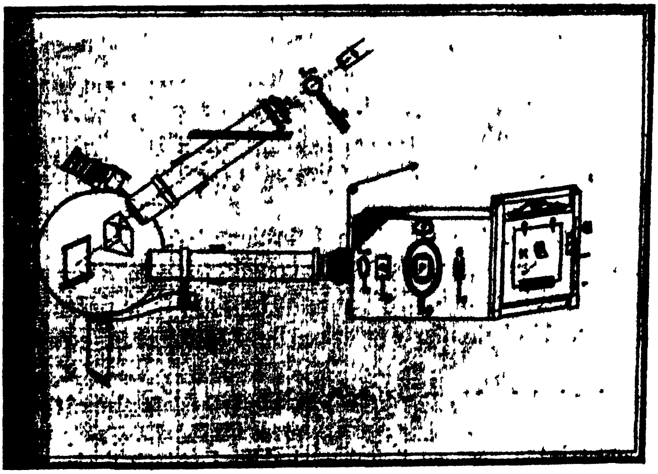
Halbschatten-vorrichtung wird erreicht, dass die eine Halfte des Gesichtsfeldes vor dem Eintritt in das absorbierende Medium in veranderlichem und messbarem Mass Schwach rechts-, die andere in davonverschiedenem Mass linkselliptisches light liefert. Durcheinem Analysator werden die Bedingungen festgestellt, under denem das Achsenverhaltniss der beiden aus dem absorbierendem Medium austretenden Strahlen jegleichen Betrag erhalt."

On a similar principle Bruhat has developed a method for measuring circular dichroism in the visible (*Bull. Soc. chim.*, 1930, **47**, 251).

Our experimental arrangement for measuring circular dichroism in the ultraviolet is given below :—

An End-on-quartz mercury lamp (S), run from a battery of 220 volts at constant current is focussed on slit S_1 of Hilger Larger Aperture Monochromator D 41, by the quartz condenser (F 278) L (vide Fig. 3). Monochromatic radiation passing through slit S_2 was converted into an approximately parallel beam by the cylindrical lens L_2 of fused quartz and focussed on the plate in the camera K. Immediately in front of this was placed the Wollaston prism Q, which gave two beams with a separation of 2·5 mm. and polarised at right angles to each other. P is the λ/4 plate manufactured by Carl Zeiss. The two beams, circularly polarised in opposite direction, were now passed through an absorption cell C of fused transparent quartz (1 cm. square × 2mm.). Between the lens L_1 and slit S_1 was fitted a graduated rotating sector (Leiss) mounted on the spindle of a motor.

FIG. 3.



Ilford process plates were used in the camera; by a rack and pinion arrangement, fitted to the carrier, fourteen impressions could be taken one above the other on the same photographic plate. Each plate contained nine impressions with water in the cell for nine different readings of the rotating sector, time-interval being the same in all cases. The remaining five impressions were taken with the cell filled with the sol matured under five different conditions. The time of exposure was regulated with an accurate metronome.

A graph was drawn by plotting log sector reading (which is proportional to log *I*, *I* being the intensity of the transmitted light) against blackening* of the corresponding impression on the plate. Fig 4 gives the nature of the graph obtained. The time of exposure with the sol in the absorption cell was so chosen that with full aperture (180°) of the rotating sector, blackening of the impressions obtained always remained in the portion of the curve AB, where it was a straight line.

The exposed plates were developed (in complete darkness) with 'Rodinal' diluted 20 times with distilled water at 18° for 5 minutes. For uniform development the bath was well placed on a shaking machine.

The plate after fixing was washed for an hour with distilled water at 18° by repeatedly changing water in the dish. The plate was dried at ordinary temperature in a large dust-free glass chamber.

The blackening of the image was measured with Zeiss photo-electric microphotometer, kept inside an air-conditioned dust-free room of low relative humidity.

The sols used were tungstic acid sol, chromic tungstate sol, vanadic acid sol, molybdic acid sol, chromic hydroxide sol and uranic acid sol. Their methods of preparation are given in Parts II, IV, VI, IX† of this paper and in a paper by Banerjee (*J. Indian Chem. Soc.*, 1937, **14**, , 59).

After mixing together the sol-forming reagents or after dialysis as the case may be, each sol was subjected to the following maturing treatment.

(1) Sol matured in the dark for a definite period.

(2) Sol matured in unpolarised light (366$\mu\mu$) for a definite period.

(3) Sol matured in plane-polarised light (366 $\mu\mu$) for a definite period.

(4) Sol matured in *l*-circularly polarised light (366 $\mu\mu$) for a definite period.

---

* Blackening is defined by $D_0 - d_1/D_0$, where D_0 is the deflection of the electrometer of the Zeiss microphotometer from its position when only the clean plate is in the path of the beam and *d*, is the deflection when a spectral line intercepts the beam.

† Part IX of this series will be published in the next issue of this Journal.

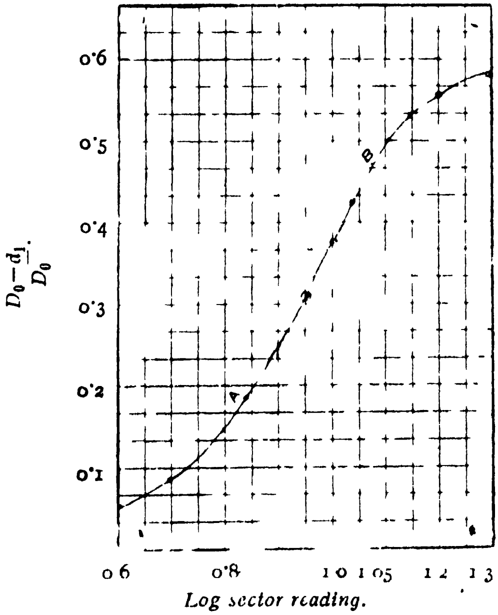
(5) Sol matured in *d*-circularly polarised light (366 $\mu\mu$) for a definite period.

For the same sol, the time of maturing was the same in all cases.

A graph was prepared for the nine impressions of each plate with water in the absorption cell by plotting log sector reading (which is proportional to the intensity of transmitted light) against the corresponding blackening. From the graph, the log intensities of transmitted light, when sols matured under the above five conditions were in the cell, were found out from the corresponding values of the blackening of the remaining five impressions on the same plate.

From the values of log sector reading, actual value of absorption coefficient of a sol can obviously be calculated if the angle of opening corresponding to each sector reading is known. 100 Divisions of the sector correspond to 180°.

FIG. 4.



The results are summarised below.

Log sector reading (d) indicates log sector reading when the incident light was *d*-circularly polarised. Log sector reading (l) indicates log sector reading when the incident light was *l*-circularly polarised. Absorption coefficient in *d*-circularly polarised light is indicated by A_d. Absorption coefficient in *l*-circularly polarised light is indicated by A^l.

TABLE I.

Molybdic Acid sol.

A. With water in the cell.

Sector reading.	Log sector reading.	D_0	D_0-d_1.	D_0-d_2.	$\frac{D_0-d_1}{D_0}$.	$\frac{D_0-d_2}{D_0}$
13	1·1139	63·9	36·0	26·9	0·563	0·421
12	1·0792	63·0	34·0	25·7	0·540	0·408
11	1·0414	61·5	29·8	20·6	0·485	0·335
10	1·0000	63·7	28·2	19·8	0·443	0·311
9	0·9542	63·0	24·5	16·2	0·390	0·257
8	0·9031	65·0	20·2	13·2	0·311	0·203
7	0·8451	64·3	15·6	9·5	0·243	0·148
6	0·7782	63 3	10·8	5·5	0·171	0·087
5	0·6990	63·5	7·2	3·9	0·113	0·061

TABLE I (*contd.*).

B. With sol in the cell.

Conc. of molybdic acid sol (in terms of molybdate equiv.) = 0·025*M*.

d (thickness of the cell) = 0·2 cm.

Nature of light in which the sol was matured for 10 hrs. immediately after mixing the reagents.	D_0.	D_0-d_1.	D_0-d_2.	$\frac{D_0-d_1}{D_0}$.	$\frac{D_0-d_2}{D_0}$.	Log sector reading (d).	(l).	Absorp. (A_l).	coefficient (A_d).	Anisotropy factor $g=\frac{A_l-A_d}{\frac{1}{2}(A_l+A_d)}$.
l-Circularly polarised	64·3	22·6	16·1	0·351	0·250	0·940	0·949	5·255	5·300	−0·0085
d-Circularly polarised	62·8	27·2	19·7	0·433	0·314	1·002	1·007	4·97	4·99	−0·0040
Plane polarised	64·3	25·9	17·3	0·403	0·269	0·972	0·966	5·17	5·14	+0·0058
Unpolarised	64·3	22·3	14·2	0·347	0·221	0·930	0·922	5·39	5·35	+0·0075
kept in the dark	64·8	25·3	17·9	0·390	0·276	0·971	0·972	5·14	5·145	−0·0009

TABLE II.

Chromic hydroxide sol.

A. With water in the cell.

Sector reading.	Log sector reading.	D_0	D_0-d_1.	D_0-d_2.	$\frac{D_0-d_1}{D_0}$	$\frac{D_0-d_2}{D_0}$.
13	1·1139	60·3	37·0	30·8	0·614	0·511
12	1·0792	60·0	35·0	28·0	0·583	0·467
11	1·0414	57·5	33·0	26·0	0·574	0·445
10	1·0000	60·3	29·7	23·1	0·493	0·383
9	0·9542	59·4	26·8	20·5	0·450	0·345
8	0·9031	61·6	26·2	19·7	0·425	0·320
7	0·8451	61·3	19·3	13·9	0·315	0·226
6	0·7782	60·0	13·2	8·9	0·220	0·148
5	0·6990	52·5	10·0	6·4	0·190	0·122

TABLE II (*contd.*).

B. With sol in the cell.

Conc. of chromic hydroxide sol (in terms of chromic equiv.) = 0·02M

d (thickness of the cell) = 0·2 cm.

Nature of light in which the sol was matured for 10 hrs. after dialysis.	D_0.	D_0-d_1.	D_0-d_2.	$\frac{D_0-d_1}{D_0}$.	$\frac{D_0-d_2}{D_0}$.	Log sector reading		Absorp coefficient		Anisotropy factor
						(d)	(l)	(A_l).	(A_d).	$g=\frac{A_l-A_d}{\frac{1}{2}(A_l+A_d)}$
l-Circulary polarised	59·7	23·5	18·8	0·394	0·315	0·916	0·924	5·38	5·42	−0·0074
d-Circularly polarised	60·6	26·2	20·6	0·432	0·340	0·949	0·952	5·24	5·256	−0·0030
Plane polarised	60·8	26·8	21·3	0·441	0·350	0·957	0·962	5·19	5·216	−0·0050
Unpolarised	61·8	24·7	20·0	0·400	0·324	0·921	0·930	5·35	5·396	−0·0086
Kept in the dark	59·2	23·7	18·7	0·400	0·316	0·921	0·926	5·37	5·396	−0·0049

TABLE III.

Uranic acid sol.

A. With water in the cell.

Sector reading.	Log sector reading.	D_0.	D_0-d_1.	D_0-d_2.	$\frac{D_0-d_1}{D_0}$.	$\frac{D_0-d_2}{D_0}$.
13	1·1139	60·3	32·7	26·4	0·542	0·438
12	1·0792	61·3	32·6	25·8	0·532	0·421
11	1·0414	60·1	28·3	22·9	0·471	0·381
10	1·0000	60·6	27·1	20·8	0·447	0·343
9	0·9542	61·2	21·0	15·0	0·343	0·245
8	0·9031	61·7	20·0	14·1	0·324	0·229
7	0·8451	59·5	12·6	8·5	0·210	0·143
6	0·7782	60·6	9·4	6·0	0·155	0·097
5	0·6990	59·8	5·3	3·5	0·0886	0·0585

TABLE III (*contd.*).

B. With sol in the cell.

Conc. of sol (as uranic acid) = 0·0183M.

d (thickness of the cell) = 0·2 cm.

Nature of light in which the sol was matured for 10 hrs immediately after preparation	D_0.	D_0-d_1.	D_0-d_2	$\frac{D_0-d_1}{D_0}$.	$\frac{D_0-d_2}{D_0}$.	Log sector reading (d).	(l).	Absorp. coeff. (A_l).	(A_d).	Anisotropy factor $g=\frac{A_l-A_d}{\frac{1}{2}(A_l-A_d)}$.
l-Circularly polarised	59·0	19·1	13·6	0·324	0·231	0·936	0·930	5·35	5·32	+0·0056
d-Circularly polarised	60·0	24·1	17·6	0·402	0·293	0·984	0·976	5·12	5·08	+0·0078
Plane polarised	59·0	18·6	13·2	0·315	0·224	0·928	0·924	5·38	5·36	+0·0037
Unpolarised	62·8	23·9	17·2	0·381	0·274	0·972	0·968	5·16	5·14	+0·0039
Kept in the dark	61·4	22·2	16·6	0·362	0·270	0·962	0·958	5·21	5·19	+0·0038

TABLE IV.

Tungstic acid sol.

A. With water in the cell.

Sector reading	Log sector reading.	D_0.	D_0-d_1	D_0-d_2.	$\frac{D_0-d_1}{D_0}$.	$\frac{D_0-d_2}{D_0}$.
13	1·1139	55·0	25·0	21·2	0·455	0·389
12	1·0792	61·5	24·2	20·0	0·394	0·326
11	1·0414	61·5	23·6	19·1	0·384	0·311
10	1·0000	60·5	21·0	15·7	0·347	0·260
9	0·9542	55·0	15·8	12·2	0·287	0·222
8	0·9031	55·5	14·2	10·2	0·256	0·187
7	0·8451	57·3	11·6	8·2	0·202	0·143
6	0·7782	54·4	8·4	4·2	0·154	0·077
5	0·6990	59·0	7·0	3·9	0·110	0·066

TABLE IV (*contd.*).

B. With sol in the cell.

Conc. of tungstic acid sol (in terms of tungstate equivalent) = 0·0125*M*. d = 0·2 cm.

Nature of light in which the sol was matured for 6 hrs. immediately after mixing the reagents.	D_0.	D_0-d_1.	D_0-d_2.	$\frac{D_0-d_1}{D_0}$.	$\frac{D_0-d_2}{D_0}$.	Log sector reading (d).	(l).	Absorp coeff. (A_l).	(A_d).	Anisotropy factor $g=\frac{A_l-A_d}{\frac{1}{2}(A_l+A_d)}$.
l-Circularly polarised	60·8	20·0	13·6	0·329	0·224	0·982	0·954	5·23	5·09	+0·0271
d-Circularly polarised	45·5	15·6	12·8	0·343	0·281	0·996	1·018	4·91	5·02	−0·0221
Plane porlarised	43·6	16·2	13·1	0·372	0·300	1·026	1·034	4·83	4·87	+0·0082
Unpolarised	51·6	15·1	10·8	0·293	0·209	0·942	0·936	5·32	5·29	−0·0056
Kept in the dark	50·6	17·4	13·2	0·344	0·261	0·998	1·000	5·01	5·001	+0·0001

TABLE V.

Vanadic acid sol.

A. With water in the cell.

Sector reading.	Log sector reading.	D_0.	D_0-d_1	D_0-d_2.	$\frac{D_0-d_1}{D_0}$	$\frac{D_0-d_2}{D_0}$.
13	1·1139	61·0	34·8	26·4	0·570	0·433
12	1·0792	64·7	33·0	25·2	0·510	0·389
11	1·0414	52·0	28·1	21·3	0·453	0·344
10	1·0000	63·1	27·0	18·9	0·428	0·300
9	0·9542	63·3	23·8	15·5	0.376	0·245
8	0·9031	61·2	18·3	12·5	0·299	0·204
7	0·8451	61·2	13·5	8·6	0·221	0·141
6	0·7782	59·9	9·3	5·9	0·155	0·099
5	0·6990	57·5	6·0	3·8	0·104	0·066

TABLE V (*contd.*).

B. With sol in the cell.

Conc. of vanadic acid sol (in terms of vanadate equiv.) = 0·0025M. d = 0·2 cm.

Nature of light in which the sol was matured for 10 hrs. immediately after mixing the reagents.	D_0.	$D_0 - d_1$.	$D_0 - d_2$.	$\frac{D_0 - d_1}{D_0}$.	$\frac{D_0 - d_2}{D_0}$.	Log sector reading (d).	(l)	Absorp coeft. (A_l)	(A_d).	Anisotropy factor $g = \frac{A_l - A_d}{\frac{1}{2}(A_l + A_d)}$.
l-Circularly polarised	63·0	17·9	10·9	0·284	0·173	0·908	0·876	5·62	5·46	+0·0289
d-Circularly polarised	59·7	15·7	11·3	0·263	0·189	0·888	0·894	5·53	5·56	−0·0054
Plane polarised	55·0	15·0	10·3	0·273	0·187	0·896	0·892	5·54	5·52	+0·0036
Unpolarised	62·7	14·8	10·3	0·236	0·164	0·866	0·860	5·70	5·67	+0·0053
Kept in the dark	69·0	16·1	10·0	0·233	0·145	0·858	0·848	5·76	5·71	+0·0087

TABLE VI.

Chromic tungstate.

A. With water in the cell.

Sector reading.	Log sector reading.	D_0.	D_0-d_1.	D_0-d_2.	$\frac{D_0-d_1}{D_0}$.	$\frac{D_0-d_2}{D_0}$.
13	1·1139	57·8	39·4	33·8	0·682	0·585
12	1·0792	60·0	38·2	32·1	0·637	0·535
11	1·0414	60·2	36·2	30·6	0·601	0·508
10	1·0000	60·6	34·3	28·1	0·566	0·464
9	0·9542	61·9	32·2	25·8	0·520	0·417
8	0·9031	59·9	30·3	23·1	0·506	0·386
7	0·8451	59·4	25·6	18·8	0·431	0·317
6	0·7782	60·0	19·3	14·4	0·322	0·2400
5	0·6990	60·2	13·8	10·0	0·229	0·166

TABLE VI (*contd.*).

B. With sol in the cell.

Conc. of chromic tungstate (in terms of tungstate equiv.) = 0·02*M*.

d (thickness of the cell) = 0·2 cm.

Nature of light in which the sol was matured for 10 hrs. immediately after mixing the reagents		D_0.	D_0-d_1	D_0-d_2.	$\frac{D_0-d_1}{D_0}$.	$\frac{D_0-d_2}{D_0}$.	Log sector reading		Absorp. coeff.		Anisotropy factor $g=\frac{A_l-A_d}{\frac{1}{2}(A_l-A_d)}$.
							(*d*).	(*l*)	(A_l).	(A_d).	
d-Circularly polarised	...	61·4	15·7	13·2	0·256	0·215	0·716	0·750	6·24	6·42	−0·0284
Plane polarised	...	59·3	15·3	10·3	0·258	0·174	0·720	0·710	6·45	6·40	+0·0077
Unpolarised	...	58·0	20·6	16·2	0·355	0·279	0·808	0·806	5·97	5·96	+0·0017
Kept in the dark	...	60·3	20·5	16·9	0·340	0·280	0·798	0·806	5·97	6·01	−0·0067

The small difference in the values of absorption coefficients for monochromatic light in the same state of polarisation exhibited by the sols (containing the same equivalent of light absorbing constituents per litre) is due to the fact that in the formation of colloids from the required ingredients, the mass and size of the colloidal particles could not be controlled to remain exactly the same in all cases.

In our results the experimental error is such that the anisotropy factor of the order of 0·008 has no significance. The anisotropy factor shown by molecular solutions investigated by Kuhn and co-workers varied from 0·005 to 0·04.

For tungstic acid sol, matured in *l*-circularly polarised llght for 6 hours, we observe a *positive* anisotropy factor, equal to 0·027 and for sol matured in *d*-circularly polarisad light, a *negative* anisotropy factor of the value of 0·0221.

For chromic tungstate acid sol, matured in *d*-circularly polarised light for 10 hours, a negative anisotropy factor, equal to 0·0284 was observed.

For vanadic acid sol, matured in *l*-circularly polarised light for 10 hours, a *positive* anisotropy factor, of the value of 0·029 was observed. In the case of vanadic acid sol, matured in *d*-circularly polarised light for 10 hours, the *negative* anisotropy factor, (equal to 0·0054), though small, indicates some positive significance and it can easily be expected that on maturing the sol in *d*-circularly polarlsed light for a longer period, it might be possible to induce anisotropy to a greater extent.

In the cases of molybdic acid sol, chromic hydroxide sol and uranic acid sol, the values of anisotropy factor are within experimental error and have no significance.

Following are the microphotographs of the plates taken in connection with the experiments on tungstic acid sol (*vide* Table IV).

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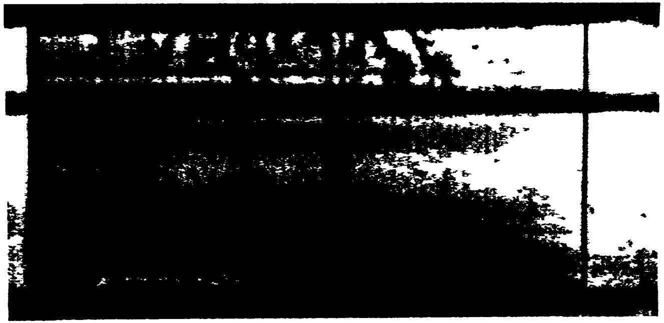
PLATE 2.

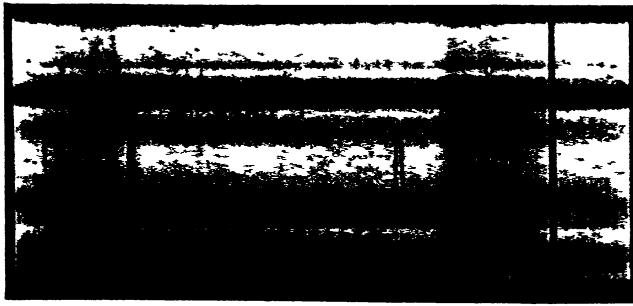
With water in the absorption cell at set [illegible]

PLATE 1



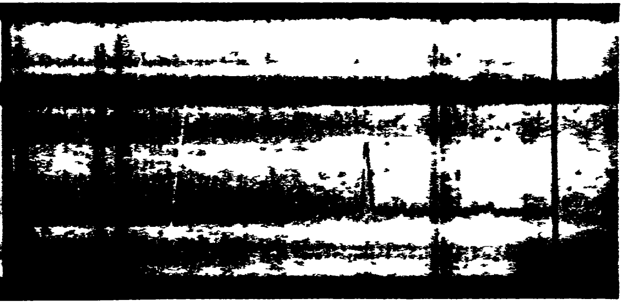
With sol pre-excited in circularly polarised light, in the absorption cell at set [illegible] reading [illegible]

PLATE 4



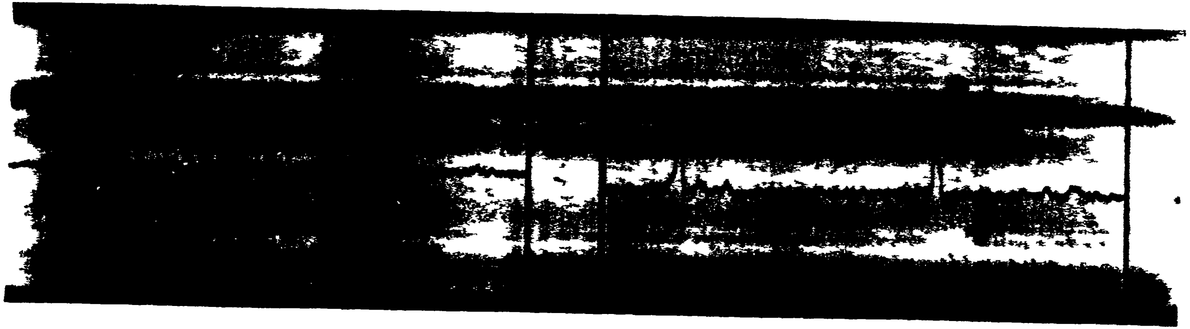
With sol pre-excited in plane polarised light in the absorption cell at set [illegible]

PLATE 3



With sol kept in the dark for [illegible] hours in the absorption [illegible]

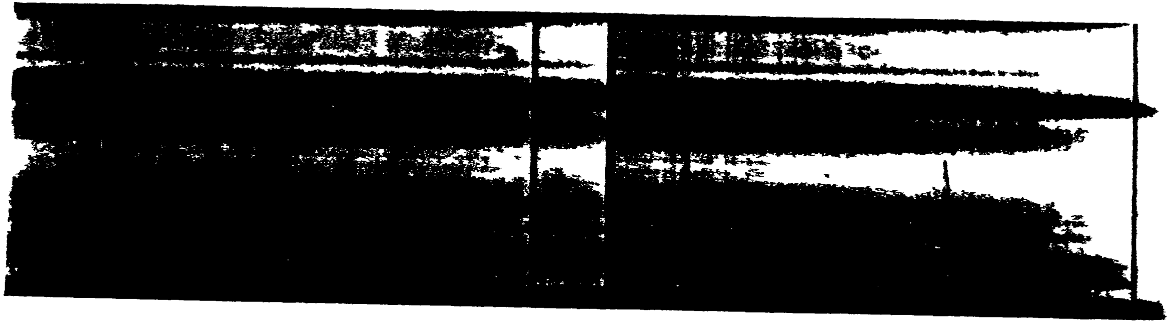
[illegible]



[illegible]

With [illegible]

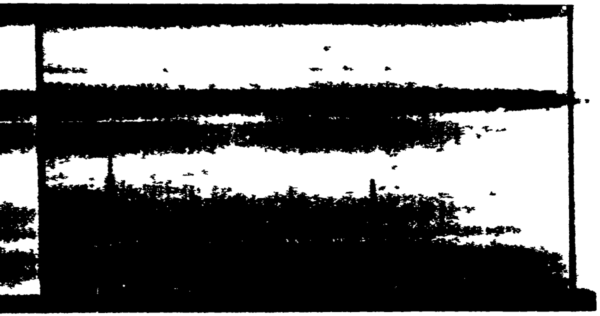
[illegible]



With [illegible]

With [illegible]

PLATE 9

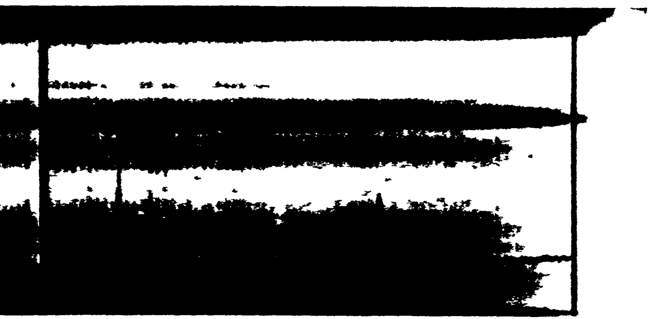


Water in the absorption [illegible] reading

PLATE 10

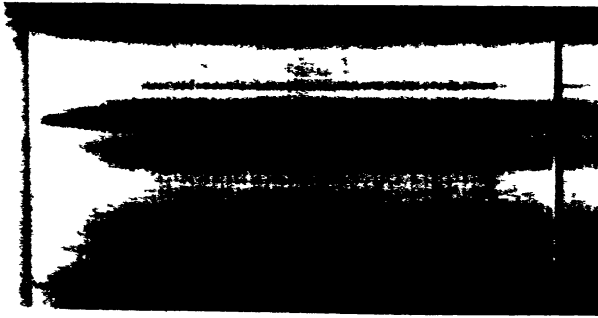
[illegible] water in the absorption cell [illegible]

PLATE 11



W[illegible] in the absorption [illegible] reading

PLATE 12



W[illegible] reading

PHOTOCHEMICAL REACTIONS WITH SOME INORGANIC COLLOIDS AS ACTIVE AGENTS UNDER THE INFLUENCE OF LIGHT IN VARIOUS STATES OF POLARISATION. PART II. PHOTOCHEMICAL REDUCTION OF TUNGSTIC ACID SOL BY GLUCOSE, LAEVULOSE, FORMALDEHYDE, LACTIC ACID, SODIUM HYPOPHOSPHITE, LEUCINE, AND GLUTAMIC ACID.

By J. C. Ghosh, T. Banerjee, S. K. Bhattacharyya and S. K. Das-Gupta.

The experimental arrangement and a portion of the experimental procedure have been described in Part I of this series. Special precautions were taken so that during the process of photoreduction, the reacting system did not come in contact with oxygen.

The sol was prepared from sodium tungstate and hydrochloric acid (Merck's reagent). In each case the amount of acid was sufficient to bring the p_H of the prepared sol to about 1·5. In case of amino-acids the reductant was dissolved in the minimum amount of hydrochloric acid (in a known volume) and the two solutions were mixed together. The sol prepared in this way showed no visible turbidity due to coagulation during the period of investigation. It is of particular importance to note that in all our experiments, the concentration of sol has been expressed in terms of the concentration of the tungstate used for the preparation of sol.

Determination of the Velocity of Reaction.

Spectrophotometric method was applied for the estimation of the reduced tungstic acid sol. For this purpose a König-Marten spectrophotometer was first calibrated in the following way :—

The cell was filled with the reaction mixture containing the reductant in excess and tungstic acid sol of known concentration and the absorption of the reaction mixture was taken in the green (525· $\mu\mu$). The corresponding reading θ_1, on the circular scale of the spectrophotometer was recorded which was evidently the zero-reading. The cell with the reaction mixture was then exposed to sunlight. After each half an hour, the absorption of the reduced tungstic acid sol was read by the spectrophotometer, the wave-length setting always remaining the same. The process was repeated until the spectrophotometer gave constant reading θ_2, which was evidently the final reading corresponding to the complete reduction of the tungstic acid sol. In this way, a set of readings θ_2 was obtained with different concentration of tungstic acid sol. The final value of θ_2 was found to be independent of p_H within the range 1·0 – 5·0.

Different concentrations of the tungstic acid sol and corresponding spectrophotometer readings θ_2, after complete reduction of the sol, are tabulated in Table I.

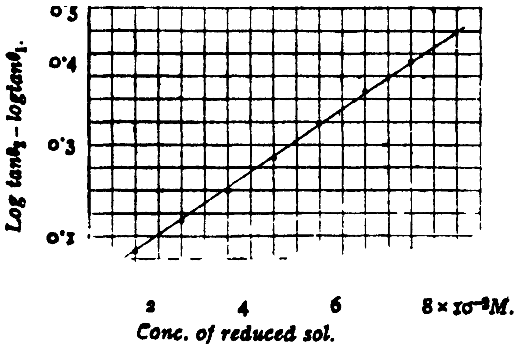
TABLE I.

Zero reading $(\theta_1) = 45°$.

Conc. of sol (*N*)	0·007	0·006	0·005	0·004	0·003	0·002	0·001
Final reading θ_2	71°·5	69°·0	65°·8	61°·5	58°·0	53°·3	48°·8
log tan θ_2 – log tan θ_1	0·4755	0·4158	0·3450	0·2652	0·2042	0·1276	0·0578

Log tan θ_2 – log tan θ_1 was plotted against the corresponding concentration of tungstic acid sol. A straight line was obtained (Fig. 1) as was to be expected. From this standard curve, the concentration of the reduced tungstic acid sol at any time during the course of our experiment was determined by taking the spectrophotometer reading at 525 $\mu\mu$.

FIG 1.



Determination of p_H.—The p_H of the reaction mixture was determined potentiometrically by using quinhydrone electrode. In cases, where concentrations of sol and reductants were varied at the same p_H, the p_H of each set of experiments was brought to the same value within ±0·01 by trial by addition of required quantities of hydrochloric acid.

Study of the Light Reaction.—Tungstic acid sol is not reduced by any of the above mentioned reductants in the dark.

Determination of the Order of Reaction.

TABLE II.

Tungstate=0·05M. Leucine=1 %. Temp.=29°·5. p_H =1·67. $I_{abs.}$=Intensity of radiation (366$\mu\mu$) absorbed in ergs per sq. cm. per sec. = 2925. d (thickness of the cell)=0·5 cm.

Time.	Spectrophotometric reading.	Conc. of reduced sol × 10^3.	$K_{\text{zero-mol.}} \times 10^9$.
(*a*) 0 min.	45°·0	0	
(*b*) 27	48°·2	0·70	0·430 (from *a* and *b*)
(*c*) 54	51°·7	1·5	0·493 (from *b* and *c*)
(*d*) 80	54°·7	2·22	0·478 (from *b* and *d*)
(*e*) 106	58°·0	3·05	0·495 (from *b* and *e*)

From the above table it is evident that the velocity constant of the photochemical reduction is zero-molecular with respect to sol. Other photoreductions also obey the zero-molecular law. The zero-molecular velocity constants have been expressed in terms of number of g. mols transformed in 1 sec. in a unit cell (1 cm. × 1 cm. × 1 cm.).

Induction Period.—In the case of leucine and sodium hypophosphite the induction period is small but in all other cases it is rather high. Passing nitrogen gas through the reaction mixture to expel dissolved oxygen has been found to diminish the induction period effectively and this has been generally done. In some cases, *e.g.*, glutamic acid where the induction period is very large (several hours) it was overcome by a preliminary exposure of the reaction mixture to total radiation of mercury lamp. The value of velocity constant noted in the following tables are those observed after the induction period is over.

Pure nitrogen was prepared by heating ammonium chloride and sodium nitrite and by passing the gas through caustic soda solution, alkaline pyrogallic acid and water.

Effect of Varying the Concentration of the Reductant.

TABLE III.

d=0·5 cm. γ=Quantum efficiency.

I_{abs} = Intensity of the absorbed radiation in ergs per sq. cm. per sec.

(*a*) Temp. = 29·5°. I_{abs} = 1166.
Tungstate = 0·05M. p_H = 1·24

Formaldehyde.

Conc. of reductant.	$K \times 10^9$.	γ.
0·8425M	1·107	1·55
0·4213	0·827	1·16
0·2106	0·552	0·78
0·1053	0·332	0·45

(*b*) Temp. = 29·5°. I_{abs} = 1432.
Tungstate = 0·05M. p_H = 1·24

Glucose.

Conc. of reductant.	$K \times 10^9$.	γ.
10%	1·007	1·15
5	0·743	0·85
2·5	0·467	0·53

(*c*) Temp. = 30°. I_{abs} = 1330.
Tungstate = 0·025M. p_H = 1·48

Laevulose.

10 %	0·898	1·11
5	0·630	0·78
2·5	0·370	0·46

(*d*) Temp. = 30°. I_{abs} = 1330.
Tungstate = ·025M. p_H = 1·18

Lactic acid.

1·01M	1·277	1·57
0·606	0·933	1·15
0·253	0·535	0·66

(*e*) Temp. = 29·5°. I_{abs} = 1330.
Tungstate = 0·025M. p_H = 1·29.

Mandelic acid.

$M/2$	0·505	0·62
$M/4$	0·483	0·60
$M/8$	0·450	0·55

(*f*) Temp. = 31°. I_{abs} = 1938
Tungstate = 0·05M. p_H = 1·72

Sodium hypophosphite.

0·0830M	1·437	1·28
0·0415	1·117	0·92
0·0207	0·772	0·64
0·0103	0·477	0·39
0·00824	0·388	0·32

(*g*) Temp. = 29·5°. I_{abs} = 2722.
Tungstate = 0·05M. p_H = 1·69

Leucine.

1·998 %	0·472	0·28
1·333	0·455	0·27
0.666	0·460	0·27
0·45	0·465	0·27

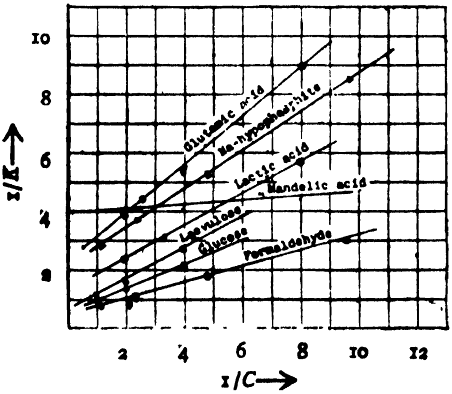
(*h*) Temp. = 29·5°. I_{abs} = 2632
Tungstate = 0·05M. p_H = 1·33

Glutamic acid.

2 %	0·260	0·16
1·5	0·227	0·14
1	0·192	0·12
0·5	0·113	0·07

In the case of leucine, the variation of concentration has got practically no effect on the reaction velocity. In all other cases, when $1/K$ is plotted against $1/C_{\text{reductant}}$, a straight line is obtained. It is to be noted however that in this case the velocity constant with only 0·4% leucine is much larger than that obtained with 2% glutamic acid (Fig. 2).

FIG. 2.



Effect of Varying the Concentration of Sol.

TABLE IV.

$d = 0·5$ cm.

Temp.	$I_{\text{abs.}}$	Tungstate.	p_H.	Reductant used.	$K_0 \times 10^{8}$.	γ.
(a)				Formaldehyde.		
29·5°	1166	0·050M	1·24	0·8425 M	1·108	1·55
,,	,,	0·0375	,,	,,	1·113	1·56
,,	,,	0·025	,,	,,	1·083	1·51
(b)				Glucose.		
29·5°	1432	0·05	1·24	10 %	1·007	1·15
,,	,,	0·0375	,,	,,	1·022	1·17
,,	,,	0·025	,,	,,	1·000	1·14
(c)				Laevulose.		
30°	1330	0·025	1·48	5 %	0·630	0·78
,,	,,	0·0125	1·47	,,	0·605	0·75
(d)				Lactic acid.		
30°	1330	0·025	1·18	1·01 M	1·277	1·57
,,	,,	0·0125	,,	,,	1·278	1·57
(e)				Mandelic acid.		
29·5°	1331	0·025	1·43	$M/4$	0·497	0·61
,,	,,	0·0125	,,	$M/4$	0·492	

TABLE IV (*contd.*).

$d = 0{\cdot}5$ cm.

Temp.	$I_{abs.}$	Tungstate.	p_H.	Reductant used.	$K_0 \times 10^9$.	γ.
(*f*)				Sodium hypophosphite.		
31°	1904	0·075 *M*	1·73	0·1245 *M*	1·675	1·38
,,	1890	0·05	,,	,,	1·608	1·36
,,	1873	0·025	,,	,,	1·525	1·31
(*g*)				Leucine.		
29·5°	2743	0·075	1·55	0·66 %	0·533	0·32
,,	2722	0·05	,,	,,	0·500	0·30
,,	2698	0·025	,,	,,	0·485	0·29
,,	2641	0·0125	,,	,,	0·467	0·28
(*h*)				Glutamic acid.		
29·5°	2677	0·075	1·33	2 %	0·272	0·16
,,	2632	0·05	,,	,,	0·260	0·16
,,	2610	0·025	,,	,,	0·250	0·15

In all cases the quantum yield of the photoreductions, under otherwise identical conditions, has been found to be practically independent of sol concentration.

Effect of Varying the Temperature.

TABLE V.

With formaldehyde.

Temp.	$I_{abs.}$	Tungstate.	p_H.	Reductant.	$K_0 \times 10^9$.	Temp. coeff. $\frac{K_{T-10}}{K_T}$.
29·5°	1620	0·025*M*	1·24	0·8425*M*	1·683	1·14
39·5	,,	,,	,,	,,	1·917	

With other reductants also, the temperature coefficient was small being of the order of 1·00–1·15.

Effect of Varying the Intensity of Radiation Absorbed.

TABLE VI.

$d = 0·5$ cm.

Temp.	$I_{abs.}$	Tungstate.	Reductant.	p_H .	$K_0 \times 10^9$.
(*a*)			**Formaldehyde.**		
29·5°	1166	0·05M	0·8425%	1·24	1·108
,,	572	,,	,,	,,	0·553
(*b*)			**Glucose.**		
29·5°	1432	0·05	10%	1·24	1·007
,,	1028	,,	,,	,,	0·775
(*c*)			**Laevulose.**		
30°	1331	0·025	5%	1·48	0·630
,,	918	,,	,,	,,	0·438
(*d*)			Lactic acid.		
30°	1331	0·025	1·01%	1·18	1·277
,,	444	,,	,,	,,	0·420
(*e*)			Mandelic acid.		
29·5°	1140	0·025	$M/4$	1·43	0·497
,,	502	,,	,,	,,	0·220
(*f*)			**Sodium hypophosphite.**		
31°	1748	0·05	0·0415N	1·76	0·975
,,	1073	,,	,,	,,	0·580
(*g*)			**Leucine.**		
29·5°	2925	0·05	0·666%	1·69	0·500
,,	1755	,,	,,	,,	0·285
(*h*)			**Glutamic acid.**		
29·5°	2632	0·05	2%	1·33	0·260
,,	1305	,,	,,	,,	0·133

The rate of reaction, under otherwise identical conditions, is proportional to the intensity of radiation absorbed.

Quantum Efficiency of the Photoreductions.

A typical example for calculating the quantum efficiency of the process is given below.

In Table II, the intensity of radiation (366 $\mu\mu$) absorbed in ergs per sq. cm. per sec. by a column of solution $0{\cdot}5$ cm thick $= 2925$ ergs

$$= \frac{2925 \times 366 \times 10^{-7}}{(6{\cdot}55 \times 10^{-27}) \times (3 \times 10^{10}) \times (6{\cdot}1 \times 10^{23})} \text{ Einsteins.}$$

$$= 8{\cdot}933 \times 10^{10} \text{ Einsteins.}$$

The zero-molecular velocity constant K (expressed in terms of no. of g. mol. transformed in sec. in a unit cell of 1 cm. × 1 cm. × 1 cm.) $= 0{\cdot}488 \times 10^{-9}$.

No. of g. mol transformed in 1 sec. in a cell of 1 cm. × 1 cm. × $0{\cdot}5$ cm

$$= 0{\cdot}244 \times 10^{-9}.$$

Quantum efficiency of the process

$$= \frac{0{\cdot}244 \times 10^{-9}}{8{\cdot}933 \times 10^{-10}}$$

$$= 0{\cdot}2735.$$

Quantum yield for the other experiments were similarly calculated.

Observations when Reactions were Carried in Polarised Light (366$\mu\mu$).

In these experiments the reacting system, immediately after mixing the reactants, was exposed to radiation polarised in the way stated, and the velocity of reaction measured after the induction period was over. In the case of exposure to *d*- or *l*-circularly polarised light, the induction period was about 8 hours.

TABLE VII.

$d = 0·5$ cm. γ = quantum efficiency

I_{abs} = Intensity of radiation absorbed per sq. cm. per sec.

(*a*) Temp. = 30°. Tungstate = 0·025*M*.
Formaldehyde = 0·8425*M*. p_H = 1·48.

State of polarisation.	I_{abs}.	$K_0 \times 10^{10}$.	γ.
l-Circularly polarised	237	1·39	0·96
d-Circularly polarised	237	0·95	0·66
Unpolarised	1170	0·65	0·93

(*b*) Temp = 29·5°. Glucose = 5%.
Tungstate = 0·025 *M*. p_H = 1·95.

State of polarisation.	I_{abs}.	$K \times 10^{10}$.	γ.
Unpolarised	1432	4·10	0·47
l-Circularly polarised	237	0·70	0·48
d-Circularly polarised	237	0·40	0·26

(*c*) Temp. = 30°. Laevulose = 5%.
Tungstate = 0·025*M*. p_H = 1·94

Unpolarised	1331	4·51	0·54
l-Circularly polarised	180	0·61	0·55
d-Circularly polarised	180	0·44	0·40

(*d*) Temp. = 30°. Lactic acid = 1·01*M*.
Tungstate = ·025*M*. p_H = 1·18

Unpolarised	1331	12·77	1·57
l-Circularly polarised	195	1·87	1·57
d-Circularly polarised	195	1·28	1·08

(*e*) Temp. = 30°. Mandelic acid = *M*/4.
Tungstate = 0·025*M*. p_H = 1·43.

Unpolarised	1331	5·0	0·61
l-Circularly polarised	328	1·22	0·61
d-Circularly polarised	328	0·87	0·43

(*f*) Temp. = 29·5°. Leucine = 0·666%.
Tungstate = 0·05*M*. p_H = 1·33

Unpolarised	2081	4·35	0·335
l-Circularly polarised	385	0·79	0·329
d-Circularly polarised	385	0·67	0·278

(*g*) Temp. = 31°. Hypophosphite = 0·12*M*.
Tungstate = 0·05*M*. p_H = 1·75.

Unpolarised	1085	8·60	1·27
l-Circularly polarised	192	1·54	1·28
d-Circularly polarised	192	1·34	1·10

(*h*) As the induction period with glutamic acid as reductant was very large (several hours), the reaction was not studied in polarised light.

It is evident from the above tables that in all cases

$$V_O = V_L > V_D ,$$

where V_O , V_L and V_D stand for velocity of reaction in unpolarised, *l*-circularly polarised and *d*-circularly polarised light respectively.

Observations on the Photoreductions with Pre-activated Tungstic Acid Sol.

Here tungstic acid sol, prepared by the action of hydrochloric acid on sodium tungstate as stated before, was first exposed in an atmosphere of nitrogen to ultraviolet rays for a sufficiently long time (about 3 hours) and mixed immediately with the reductant. The reaction (photoreduction) was then allowed to proceed in the ultraviolet light ($366\mu\mu$) also in an atmosphere of nitrogen.

TABLE VIII.

$d = 0{\cdot}5$ cm. Tungstate $= 0{\cdot}025M$. Glucose $= 10\%$. $I_{abs} = 585$.
$p_H = 1{\cdot}24$. Temp. $= 31°$.

Time.	Conc. of reduced tungstate × 10^3.	$K_0 \times 10^9$.	γ.
(1) 0 sec.	0		
(2) 32	0·89	0·462 (from 1 & 2)	1·25
(3) 64	1·72	0·447 (from 1 & 3)	
(4) 96	2·55	0·442 (from 1 & 4)	
(5) 122	3·25	0·443 (from 1 & 5)	
	Mean.	0·448	

We have noticed before that when unactivated sol was used, the reaction was zero-molecular and attended with a large initial period of induction even when the reaction proceeded in an atmosphere of nitrogen. On using the pre-activated sol in an atmosphere of nitrogen, the order of reaction remained the same but the induction period was eliminated completely. It must be noted that if the reaction proceeded in presence of air, pre-activation of the sol alone can not totally eliminate the induction period.

Table IX shows that by the process of pre-activation, the quantum efficiency is not modified to an appreciable extent.

TABLE IX.

Temp. = 31°. Tungstate = 0·025M. Glucose = 10%.

Nature of sol used.	I_{abs}	p_H.	$K_0 \times 10^9$.	γ.
Not preactivated	2440	1·25	1·717	1·13
Pre-activated	585	1·24	0·448	1·25

DISCUSSION.

The reactions have the following characteristics :—

(1) It is zero-molecular with respect to the sol. The concentration of sol within the limit studied in our experiments having practically no influence on the quantum efficiency of the photochemical process and the absorption of radiation 366$\mu\mu$ by sol within this limit is practically complete.

(2) Zero-molecular velocity constant is proportional to the light energy absorbed.

(3) Quantum yield of the photochemical process varies practically between 1 and 0·1.

(4) The inverse of the velocity constant plotted against the inverse of the concentration of reductant gives a straight line.

(5) The temperature coefficient of the velocity constant is nearly unity.

(6) *l*-Circularly polarised light gives a higher quantum yield under otherwise identical conditions than the *d*-circularly polarised light.

All these characteristic features can be explained by the assumption that radiations absorbed by tungstic acid particles on the sol surface create active centres for oxidation on that surface. If within the life period of these active centres, a molecule of reductant collides with them it undergoes oxidation.

The rate of reaction is proportional to the number of such active centres created per second and the surface concentration of the reductant.

Hence $dx/dt = 1/Nh\nu \times C_s^R$

where C_s^R is the surface concentration of reductants.

But according to Langmuir's hypothesis, surface concentration of the reductant is

$$\frac{K_1 C_s^R}{K_2 C_s^R + 1}$$

where C_s^R is the concentration of the reductants in the solution.

Therefore, $$dx/dt = \frac{1}{Nh\nu} \times \frac{K_1 C_s^R}{1 + K_2 C_s^R}$$

or $$\frac{1}{dx/dt} = \frac{Nh\nu}{1}\left[\frac{K_2}{K_1} + \frac{1}{K_1 C_s^R}\right] = \left[\frac{1}{K} + \frac{1}{K' C_s^R}\right]$$

for constant value of $\frac{1}{Nh\nu}$

We have already seen that the inverse of the velocity constant plotted against the inverse of the concentration of the reductant is a straight line as is demanded by the above equation.

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Received July 20, 1936.

PHOTOCHEMICAL REACTIONS WITH SOME INORGANIC COLLOIDS AS ACTIVE AGENTS UNDER THE INFLUENCE OF LIGHT IN VARIOUS STATES OF POLARISATION. PART III. ON THE EFFECT OF p_H ON THE PHOTO-REDUCTION OF TUNGSTIC ACID SOL IN UNPOLARISED LIGHT.

By J. C. Ghosh, T. Banerjee and Md. Surat Ali Khan.

The present section deals with the effect of p_H on the velocity of photoreduction of tungstic acid sol. For purposes of comparison, the effect of p_H on the velocity of reaction with three types of reductants *viz.*, electrolytes, non-electrolytes, and ampholytes has been studied.

EXPERIMENTAL.

Preparation of Sol.—The sol was prepared exactly in the same way as before and for variation of p_H of the reaction mixture, solutions of hydrochloric acid or caustic soda (Merck's reagent) were subsequently added as the case may be. This procedure is necessary to ensure the complete formation of the sol. The p_H of the reaction mixture was brought by trial to the required value.

The p_H values were measured by the quinhydrone electrode.

Experimental results.—The effect of the change in the concentration of sodium chloride, formed during neutralisation of acid by NaOH for regulating the p_H, on the velocity of reaction was first studied and found to be nil.

Effect of p_H on the Velocity of Photoreduction.

TABLE I.

d (thickness of the cell)=0.5 cm., γ=Quantum efficiency. I_{abs}= Intensity of absorbed radiation in ergs/cm^2/sec.

(*a*) Tungstate=0·05*M*. Formaldehyde=0·8425*M*. $I_{abs.}$ (366$\mu\mu$)=1166. Temp.=29·5°.

p_H ...	1·48	1·60	2·12	4·08
$K_0 \times 10^{10}$ ...	6·50	6·42	3·64	2·27
γ ...	0·91	0·76	0·51	0·32

TABLE I (*contd.*).

(*b*) **Tungstate** = 0·025M. **Glucose** = 10%. I_{abs} = 2440. **Temp.** = 31°.

p_H	... 1·25	1·50	1·73	1·82	2·12	2·61	4·01
$K_0 \times 10^{10}$	.. 17·17	15·17	10·42	9·92	8·42	5·60	1·53
γ	... 1·13	0·99	0·68	0·65	0·55	0·37	0·10

(*c*) **Tungstate** = 0·025M. **Laevulose** = 5%. I_{abs} = 1331. **Temp.** = 30°.

p_H	... 1·35	1·48	1·94	2·12
$K_0 \times 10^{10}$	... 8·68	6·30	4·50	3·98
γ	... 1·07	0·78	0·55	0·49

(*d*) **Tungstate** = 0·025M. **Lactic acid** = 1·01M. I_{abs} = 1331 **Temp.** = 30°.

p_H	... 0·76	0·85	1·06	1·18	1·61	2·12	2·52
$K_0 \times 10^{10}$	.. 9·83	12·03	12·78	12·77	8·70	5·53	3·98
γ	... 1·21	1·48	1·57	1·57	1·07	0·68	0·49

(*e*) **Tungstate** = 0·025M. **Mandelic acid** = $M/4$. I_{abs} = 1331. **Temp.** = 29·5°.

p_H	... 1·13	1·32	1·62	2·12	2·3
$K_0 \times 10^{10}$	... 4·57	4·83	3·70	2·76	2·35
γ	... 0·56	0·59	0·46	0·34	0·29

(*f*) **Tungstate** = 0·05M. **Leucine** = 0·666%. I_{abs} = 2722. **Temp.** = 29·5°.

p_H	... 1·31	1·65	1·86	2·33	2·98
$K_0 \times 10^{10}$	... 5·67	4·60	3·33	1·58	0·87
γ	... 0·332	0·27	0·196	0·093	0·051

(*g*) **Tungstate** = 0·05M. **Glutamic acid** = 1%. I_{abs} = 2632. **Temp** = 29·5°

p_H	... 1·40	1·52	1·74	2·05	2·51
$K_0 \times 10^{10}$	... 2·20	1·97	1·28	0·67	0·42
γ	... 0·134	0·120	0·078	0·040	0·025

(*h*) **Tungstate** = 0·05M. **Hypophosphite** = 0·083M. I_{abs} = 1748. **Temp.** = 31°.

p_H	... 1·75	2·21	2·58	3·50	4·10
$K_0 \times 10^{10}$	... 12·83	9·75	7·35	3·35	1·67
γ	... 1·17	0·89	0·67	0·31	0·15

DISCUSSION.

From Figs. 1 and 2, it is evident that in all cases at about p_H 4·8, the velocity of reaction is practically nil. Then with the decrease of p_H, the velocity of reaction increases steadily. After the p_H reaches 1.3, the system becomes unstable and the colloid coagulates shortly after its preparation.

FIG. 1.

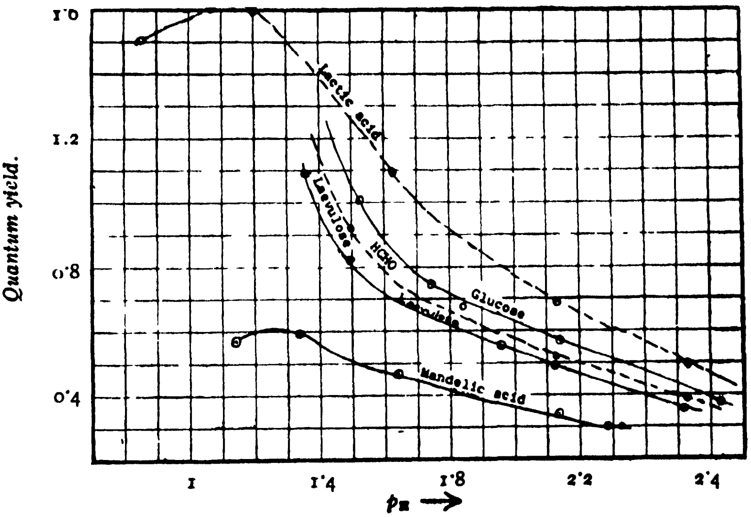


FIG. 2.

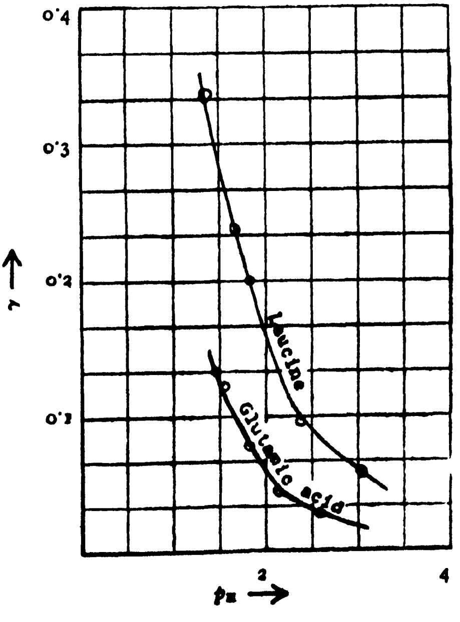
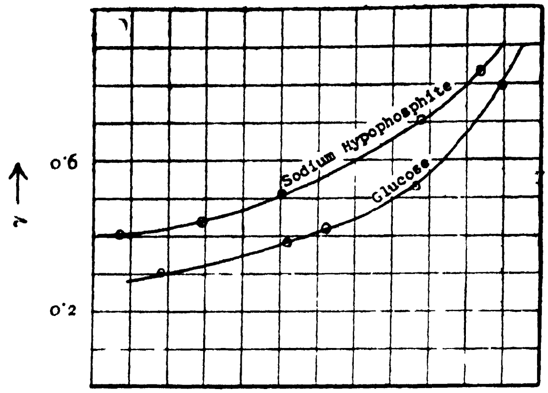


FIG. 3.



Our results can be best explained on the basis of the observations made by Rabinowitsch and Kargin (*Z. physikal. Chem.*, 1931, **152**, 26) and G. Jander and others (*Z. anorg. Chem.*, 1929, **180**, 138).

Rabinowitsch (*loc. cit.*) from the measurement of specific conductivity of tungstic acid sol at different dilutions came to the conclusion that above p_H 4·8, tungstic acid sol was in state of molecular dispersion. In other words tungstic acid sol formed a true solution. Below p_H 4·8, colloidal micelles are formed. As the p_H is still decreased, the portion of tungstic acid existting as micelles increases.

That the increase in the velocity of reaction is due to the increase in concentration of micelles can be clearly seen from the data recorded in Table II.

TABLE II.

(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)
p_H.	γ_{Glucose}.	γ_{HCHO}.	$\gamma_{\text{Laevulose}}$.	$\gamma_{\text{Lactic acid}}$.	$\gamma_{\text{Mandelic acid}}$.	E/A.	F/A.	G/A.	H/A
	(A)	(E)	(F)	(G)	(H)				
2·5	0·40	0·375	0·35	0·50	0·25	0·90	0·84	1·21	0·60
2·25	0·485	0·455	0·43	0·615	0.30	0·90	0·85	1·22	0·59
2·0	0·585	0·555	0·525	0·74	0·355	0·95	0·89	1·26	0·61
1·75	0·70	0·655	0·62	0·92	0·42	0·91	0·87	1·29	0·59
1·5	0·995	0·895	0·80	1·24	0·53	0·90	0·80	1·24	0·53

If we compare the relative rate of increase in quantum yield with laevulose, glucose, etc. in Table II, we find that the ratio between quantum yield at different p_H is practically constant (*vide* columns 7, 8, 9 and 10, Table II).

It may be pointed out that lactic acid and mandelic acid between p_H 1·5 and 2·5 exist practically in the undissociated state.

Lactic acid and mandelic acid stabilise tungstic acid sol below p_H 1·5 but at the same time, the effective specific surface of the sol is much diminished due to increase in the size of the colloidal micelles. So we get a diminution in the velocity in those cases where it is possible to keep the reaction mixture stable below 1·5.

TABLE III.

γ=Quantum efficiency.

p_H	4·0	3·75	3·5	3·25	3·0	2·75	2·5	2·25	2·0	1·75
$\gamma_{\text{Hypophosphite}}$	0·175	0·235	0·30	0·37	0·465	0·58	0·70	0·845	0·985	1·15
γ_{Glucose}	0·105	0·135	0·18	0·22	0·275	0·335	0·40	0·485	0·58	0·70
$\frac{\gamma_H}{\gamma_G}$*	1·67	1·74	1·67	1·68	1·70	1·73	1·75	1·74	1·70	1·65

We know that hypophosphite dissociates more and more as p_H increases. The constancy of the ratio γ_H/γ_G in Table III indicates that the undissociated or the dissociated hypophosphite has the same effect on the velocity of photoreduction of tungstic acid sol.

TABLE IV.

(1) p_H.	(2) γ_{Glucose}. (A)	(3) γ_{Leucine} (C)	(4) $\gamma_{\text{Glutamic acid}}$. (D)	(5) C/A.	(6) D/A.
4·0	0·105	0·02	...	0·19	...
3·75	0·135	0·028	0·008	0·21	0·06
3·5	0·180	0·037	0·012	0·20	0·063
3·25	0·220	0·045	0·015	0·202	0·067
3·0	0·275	0·054	0·018	0·20	0·067
2·75	0·335	0·065	0·022	0·18	0·067
2·5	0·40	0·078	0·027	0·20	0·067
2·0	0·58	0·142	0·045	0·24	0·080
1·75	0·70	0·237	0·070	0·33	0·100
1·5	0·995	0·31	0·12	0·31	0·12

---

* γ_H & γ_G denote respectively γ due to hypophosphite and glucose.

In the case of amino-acids (Table IV), the rate of reaction (hence quantum yield) is influenced by a second factor, in addition to the effect of H^+ ions on the tungstic acid sol. We observe from Table IV, columns (5) and (6), that in the case of leucine and glutamic acid, the relative increase in reaction velocity with decrease in p_H is different from that obtained with glucose as reductant.

The abnormal increase in reaction rate as p_H is lowered can be explained in the following manner.

The velocity of the photoreduction with amino-acids as reducing agent can be expressed by the equation

$$dx/dt = K_1 \text{ (surface conc. of } NH_2{\cdot}R{\cdot}COOH) + K_2 \text{ (surface conc. of } {}^+NH_3{\cdot}R{\cdot}COOH)$$

It is the positively charged ${}^+NH_3{\cdot}R{\cdot}COOH$ and the neutral molecule or the zwitter ion $[{}^+NH_2{\cdot}R{\cdot}COO^-]$ which alone can get adsorbed on the negatively charged micelle surface.

The concentration of the ions ${}^+NH_3{\cdot}R{\cdot}COOH$ in a solution of amino-acids, increases rapidly (*vide* Table V) as the p_H is decreased below p_H about 3·0 (Harris, *Proc. Roy. Soc.*, 1924, **B95**, 441).

Assuming that the adsorbability of the " zwitter ion " and the form ${}^+XH$ on the surface of the sol micelles is of the same order and remembering that at the same p_H for leucine, the velocity constant is independent of the concentration of leucine, we may express the velocity constant of the reaction by an equation of the type

$$\frac{dx}{dt} = K_1 \frac{C\,[{}^+X^-]}{C_{total}} + K_2 \frac{C\,[{}^+XH]}{C_{total}}.$$

K_1 is a function of p_H which determines the reactive capacity of colloidal micelles. At p_H 4·0, leucine exists practically in the form ${}^+X^-$ and K_1 has the value 0·02. It is to be expected that the variation of K_1 with p_H should be the same as that observed in the case of glucose. Similarly K_2 is another function of p_H, being equal to 0·31 at p_H 1·5 where leucine exists practically in the ${}^+XH$ form and decreases with p_H at the rate at which the velocity of oxidation of glucosse by tungtic acid sol decreases with p_H.

$C_{[^+X^-]}$, $C_{[^+XH]}$ and C_{total} denote the concentrations of $[^+X^-]$, $[^+XH]$ and total concentration of amino-acid used in the experiment.

Similar equation was applied in the case of glutamic acid. The agreement between the observed and calculated values indicates that our assumptions are justified.

TABLE V.

K_B

$$K_a = \frac{K_W}{K_B} = \frac{[^+X^-]\,[H^+]}{^+[XH]}.$$

Leucine $= 2{\cdot}3 \times 10^{-12}$

Glutamic acid $= 1{\cdot}5 \times 20^{-12}$ $\quad 4{\cdot}348 \times 10^{-3}$

$6{\cdot}667 \times 10^{-3}$

(L. J. Harris, *loc. cit.*)

	Leucine.		Glutamic acid.	
p_H.	$C_{[^+X^-]}$.	$C_{[^+XH]}$.	$C_{[^+X^-]}$.	$C_{[^+XH]}$.
1·5	0·081	0·589	0·174	0·826
1·75	0·132	0·538	0·273	0·727
2·0	0·203	0·467	0·400	0·600
2·25	0·292	0·378	0·543	0·457
2·50	0·388	0·282	0·698	0·302
2·75	0·476	0·184	0·789	0·211
3·0	0·545	0·125	0·870	0·130
3·25	0·593	0·077	0·922.	0·078
3·50	0·625	0·045	0·955	0·045
3·75	0·644	0·026	0·974	0·026
4·0	0·655	0·015	0·985	0·015

The results are plotted graphically in Figs. 4 and 5.

Fig. 4.

Glutamic acid.

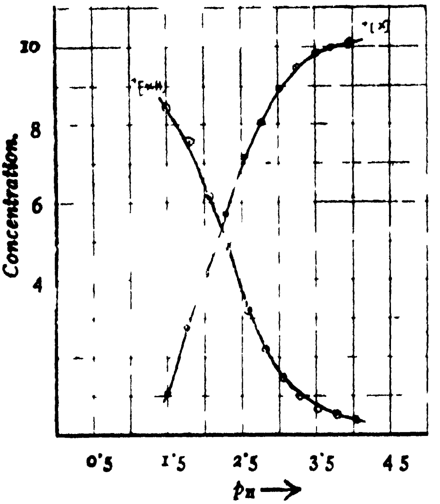


Fig. 5.

Leucine.

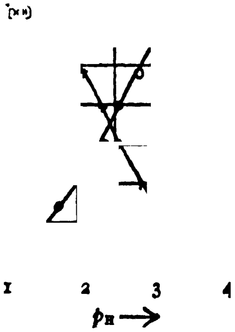


TABLE VI.

p_H.	Leucine. K_1.	K_2.	dx/dt calc.	(obs.).	Glutamic acid. K_1.	K_2.	dx/dt calc.	(obs.).
4·00	0·02	0·0326	0·0203	0·02				
3·75	0·0257	0·0419	0·0263	0·028	0·008	0·0163	0·0082	0·008
3·50	0·0343	0·0559	0·0351	0·037	0·108	0·0217	0·0112	0·012
3·25	0·0419	0·0684	0·0449	0·045	0·013	0·0265	0·0141	0·015
3·00	0·0524	0·0855	0·0586	0·054	0·0163	0·0332	0·0185	0·018
2·75	0·0638	0·0942	0·0712	0·065	0·0199	0·0404	0·0242	0·022
2·50	0·0769	0·124	0·0967	0·078	0·0237	0·0482	0·0311	0·027
2·00	0·011	0·180	0·159	0·142	0·0344	0·0700	0·0557	0·045
1·75	0·123	0·218	0·199	0·237	0·0415	0·0844	0·0727	0·071
1·50	0·190	0·310	0·300	0·310	0·059	0·1200	0·110	0·12

On decreasing the p_H we have observed that beyond p_H 1·3, the system becomes unstable, the sol being coagulated. This corroborates the observation of Jander (*loc. cit.*) who found that tungstic acid micelle is coagulated at p_H 1·5 ± ·2.

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PHOTOCHEMICAL REACTIONS WITH SOME INORGANIC COLLOIDS AS ACTIVE AGENTS UNDER THE INFLUENCE OF LIGHT IN VARIOUS STATES OF POLARISATION PART IV. PHOTO-CHEMICAL REDUCTION OF MOLYBDIC ACID SOL BY GLUCOSE, FORMALDEHYDE, ETHYL ALCOHOL, SODIUM HYPOPHOSPHITE, LEUCINE, GLUTAMIC ACID, AND α-ALANINE.

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The experimental arrangement was the same as before.

The sol was prepared from ammonium molybdate (Merck's reagent) and hydrochloric acid (Merck's reagent). Estimation of the reduced molybdic acid sol was carried out by spectrophotometric method using König-Marten spectrophotometer which was calibrated similarly as described in Part II. The absorption was noted in the green (525 μμ). Results of calibration (*vide* Fig. 1) are tabulated below.

TABLE I.

Molybdate.	Zero-reading. θ_1	Final reading. θ_2	Log tan θ_2 − log tan θ_1.
0·004 *M*	45°·0	72°·5	0·5013
0·0035	,,	70°·5	0·4389
0·0030	,,	67°·5	0·3828
0·0025	,,	64°·0	0·3118
0·0020	,,	60°·0	0·2386
0·0010	,,	53°·5	0·1308

The concentration of the sol was expressed in terms of the molybdate used for the preparation of the sol and for calculating it the unit used was one-seventh of the molecular weight of the ordinary ammonium molybdate $[(NH_4)_6 Mo_7O_{24}, 4 H_2O]$.

FIG. 1.

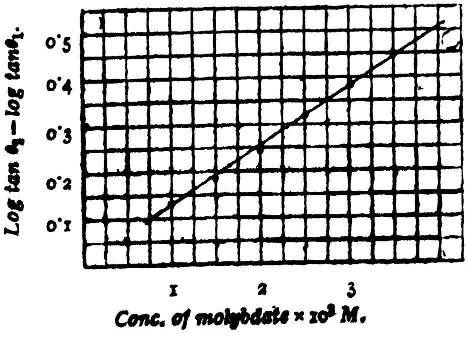
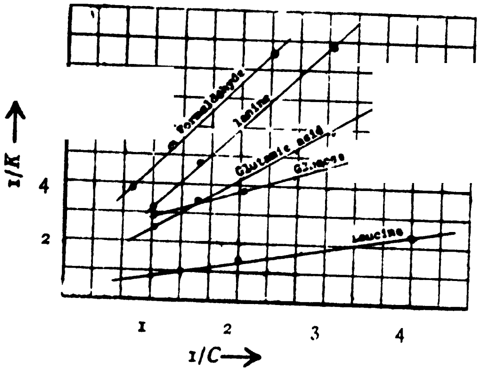


FIG. 2.



Experimental Results.

Molybdic acid sol is not reduced by glucose, formaldehyde, alcohol, leucine, glutamic acid and α-alanine in the dark, but is reduced by hypophosphite in the dark when the p_H is below 3·9 In the case of hypophosphite the dark reaction begins instantaneously on mixing the sol with the reductant. The velocity of the dark reaction and the light reaction (in all cases) is zero-molecular with respect to the sol. The following is a special example for illustration.

TABLE II.

Leucine = 1%. Sol = 0·05M. p_H = 2·46. Temp. = 29·5.° I_{abs} = 3150 ergs/sq. cm./sec. (366$\mu\mu$). d (thickness of the reaction cell) = 0·5 cm.

	Time.	Spectrophotometric reading.	Conc. of reduced sol.	$K_{zero\text{-}mol} \times 10^9$.
(*a*)	0 min.	45°	...	...
(*b*)	30	49°·5	$0{\cdot}55 \times 10^{-3}M$	0·305 (from *a* & *b*)
(*c*)	46	56°·0	$1{\cdot}35 \times 10^{-3}$	0·833 (from *b* & *c*)
(*d*)	62	61°·2	$2{\cdot}08 \times 10^{-3}$	0·797 (from *b* & *d*)
(*e*)	73	65°·0	$2{\cdot}65 \times 10^{-3}$	0·813 (from *b* & *e*)
				mean of the last three = 0·184

Induction Period.—All the reactions are attended with induction period. Passing nitrogen through the reaction mixture partially eliminated the induction period. In case of glutamic acid and α-alanine, the induction period is very high (3-4 hours) and it was overcome by exposing the reaction mixture first to the total radiation of the mercury lamp.

Effect of Varying the Concentration of Reductant.

TABLE III A.

$d = 0·5$ cm. γ = Quantum efficiency.

Temp.	I_{abs} (366$\mu\mu$)	Molybdate.	p_H.	Conc. of reductant.	$K. \times 10^9$.	γ.
(*a*)				Formaldehyde.		
31°	307·7	0·018*M*	2·7	1·275*M*	0·275	1·48
,,	,,	,,	,,	0·85	0·194	1·03
,,	,,	,,	,,	0·43	0·119	0·63
(*b*)				Glucose.		
31°	483	0·018	1·7	20%	0·365	1·24
,,	,,	,,	,,	10	0·270	0·92
,,	,,	,,	,,	5	0·184	0·62
(*c*)				Leucine.		
29·5°	3150	0·05	1·78	2%	1·270	0·652
,,	,,	,,	,,	1·5	0·967	0·495
,,	,,	,,	,,	1	0·720	0·369
,,	,,	,,	,,	0·5	0·425	0·218
(*d*)				Glutamic acid.		
29·5°	3825	0·05	1·75	1%	0·202	0·085
,,	,,	,,	,,	0·667	0·152	0·064
,,	,,	,,	,,	0·333	0·088	0·037
(*e*)				α-Alanine.		
29·5°	2812	0·05	2·05	1%	0·168	0·097
,,	,,		,,	0·667	0·108	0·062
,,	,,	,	,,	0·333	0·058	0·033

$1/K$ plotted against $1/C_{\text{reductant}}$ gives a straight line in each case (Fig. 2).

TABLE III B.

Reductant used = Sodium hypophosphite. Temp. = 31°.

I_{abs} = 1696· p_H = 1·80.

Molybdate.	Reductant.	$K_{total} \times 10^9$. (K_t)	$K_{dark} \times 10^9$. (K_d)	$K_{light} \times 10^9 =$ $(K_t - K_d) \times 10^9$.	γ.
0·05M	0·083N	0·867	0·350	0·517	0·485
,,	0·0415	0·438	0·173	0·265	0·250
,,	0·0207	0·210	0·082	0·128	0·121

The above data indicate that both the dark and light reactions are proportional to the concentration of the reductant.

Effect of Varying the Concentration of Sol.

TABLE IV A.

Reductant used = 0·083M-Sodium hypophosphite. Temp. = 31°.

p_H = 2·15. d = 0·5 cm.

Molybdate.	I_{abs} (366$\mu\mu$)	$K_{total} \times 10^9$. (K_t)	$K_{dark} \times 10^9$. (K_d)	$K_{light} \times 10^9$ $(K_t - K_d) \times 10^9$.	$\gamma_{(366\mu\mu)}$.
0·1M	1678	0·742	0·317	0·425	0·405
0·075	1488	0·608	0·236	0·372	0·400
0·05	1257	0·483	0·167	0·316	0·393
0·025	1070	0·358	0·087	0·271	0·405

Therefore, it is evident that the quantum yield of the photochemical reaction is independent of the concentration of sol and the velocity of dark reaction is approximately proportional to the concentration of sol.

TABLE IVB.

$d = 0\cdot5$ cm.

Temp.	I	Molybdate.	p_H.	Reductant.	$K_0 \times 10^9$.	γ (366μμ)
(a)				Formaldehyde.		
31°	570·7	0·018M	2·7	0·85M	0·488	1·40
,,	662·5	0·036	,,	,,	0·569	1·41
(b)				Glucose.		
31°	263·4	0·018	1·7	10%	0·148	0·92
,,	333·7	0·027	,,	,,	0·188	0·92
,,	380·4	0·036	,,	,,	0·214	0·92
(c)				Leucine.		
29·5°	1575	0·01	1·24	1%	0·212	0·215
,,	3150	0·05	,,	,,	0·442	0·226
,,	3825	0·075	,,	,,	0·535	0·224
(d)				α-Alanine.		
29·5°	1710	0·0125	2·05	1%	0·103	0·097
,,	2317	0·025	,,	,,	0·143	0·099
,,	2812	0·05	,,	,,	0·168	0·097
(e)				Glutamic acid.		
29·5°	1912	0·0125	1·62	1%	0·085	0·072
,,	2992	0·025	,,	,,	0·137	0·073
,,	3825	0·05	,,	,,	0·180	0·075

In each case the quantum yield of the photochemical reaction is independent of the concentration of the sol.

Temperature Coefficient.

In all cases the temperature coefficient of the photochemical process $\left(\frac{K_{T+10}}{K_T}\right)$ is small being of the order of unity. The temperature coefficient of the dark reaction with hypophosphorous acid is of the order of 2 as will be evident from the following table.

TABLE V.

Sodium hypophosphite=0·083*N*. p_H =1·63.

Molybdate=0·05*M*. I_{abs} =1696.

Temp.	K_{total} (K_t)	K_{dark} (K_d)	K_{light}= (K_t-K_d)	Temp. co-eff. (light reaction).	Temp. coeff. (dark reaction).
41°	1·683	0·962	0·722	1·02	2·04
31°	1·177	0·473	0·703	,,	,,

Variation of Intensity of Incident Radiation.

TABLE VI.

Temp.	I_{abs}.	Molybdate.	p_H.	Reductant.	$K\times10^9$	I/I_2.	$\frac{K_1}{K_2}$.
a)				Formaldehyde.			
31°	998·1	·018*M*	2·7	0·85*M*	0·888	1·75	1·82
,,	570·7	,,	,,	,,	0·488		
b)				Glucose.			
31°	482·9	0·018	1·7	10%	0·270	1·83	1·82
,,	263·4	0·018	,,	,,	0·148		
(*c*)				Hypophosphite.			
31°	1246	0·05	1·85	0·0415*N*	0·200	1·71	1·66
,,	727	,,	,,	,,	0·120		
(*d*)				Leucine.			
29·5°	2475	0·05	2·28	1%	0·685	1·80	1·74
	1372	,,	,,	,,	0·393		
(*e*)				α-Alanine.			
29·5°	2812	0·05	2·6	1%	0·215	1·75	1·86
,,	1605	,,	,,	,,	0·115		
(*f*)				Glutamic acid.			
29·5°	2812	0·05	2·31	0·667%	0·167	1·66	1·69
,,	1687	,,	,,	,,	0·098		

The rate of reaction under otherwise identical conditions is proportional to intensity of radiation absorbed.

Quantum Efficiency of the Process.—The quantum efficiencies of the process have been calculated exactly as done in Part II of this series and are given in Table IIIA.

Effect of Polarised Light (366$\mu\mu$).

TABLE VII.

$d = 0·5$ cm.

Nature of light.	I_{abs}.	$K_0 \times 10^9$.	$K' \times 10^9$.
(*a*) Temp. = 31°. Formaldehyde = 0·85M. Molybdate = 0·018M p_H = 2·7			
Ordinary	570·7	0·489	0·066
d-Circularly polarised	76·8	0·066	
l-Circularly polarised	76·8	0·067	
(*b*) Temp. = 31°. Glucose = 10%. Molybdate = 0·018M. p_H = 2·7.			
Ordinary	482·9	0·296	0·048
d-Circularly polarised	76·8	0·051	
l-Circularly polarised	76·8	0·052	
(*c*) Temp. = 31°. Alcohol = 10·4M. Molybdate = 0·018M. p_H = 2·7.			
d-Circularly polarised	109·8	0·017	
l-Circularly polarised	109·8	0·018	
(*d*) Temp. = 29°·5. Leucine = 1%. Molybdate = 0·05M. p^H = 2·13.			
Ordinary	2475	0·663	0·116
d-Circularly polarised	433	0·116	
l-Circularly polarised	433	0·118	

K' in column (4) has been calculated for the intensity at which the reaction was carried in circularly polarised light, assuming that the velocity constant varies directly as the intensity of absorbed radiation.

From Table VII, it is evident that $V_O = V_L = V_D$, the terms having the same significance as in Part II of this series.

DISCUSSION.

The reactions have the following characteristics :—

(1) It is zero-molecular with respect to sol and the concentration of the sol has got no influence on the quantum efficiency of the photochemical process.

(2) Zero-molecular velocity constant is proportional to the absorbed radiation.

(3) Maximum value of the quantum yield observed is practically unity.

(4) The inverse of velocity constant plotted against the inverse of the concentration of the reductant gives a straight line. (In case of hypophosphite, dark reaction is proportional both to the concentration of sol and that of hypophosphorous acid).

(5) Temperature coefficient of the velocity constant is unity

$$\frac{K_{T+10}}{K_T} = 1{\cdot}02.$$

(6) *d*- and *l*-circularly polarised light are equally effective (*cf.* reduction of tungstic acid sol; Part II).

All these characteristic features can be explained by the assumptions which were similar to that in the case of tungstic acid sol in Part II.

Unlike the reduction of tungstic acid sol, *d*- and *l*- circularly polarised lights are equally effective.

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PHOTOCHEMICAL REACTIONS WITH SOME INORGANIC COLLOIDS AS ACTIVE AGENTS UNDER THE INFLUENCE OF LIGHT IN VARIOUS STATES OF POLARISATION. PART V. ON THE EFFECT OF p_H ON THE PHOTOREDUCTION OF MOLYBDIC ACID SOL IN UNPOLARISED LIGHT.

By J. C. Ghosh, T. Banerjee and Md. S. A. Khan.

The present section deals with the effect of p on the velocity of reduction of molybdic acid sol. The reductants studied were mostly those used in the analogous reaction with tungstic acid sol.

EXPERIMENTAL.

Experimental procedure and arrangments of apparatus are exactly the same as in Part IV.

Sodium chloride of different concentrations, as formed during the process of neutralisation of acid by caustic soda for changing the p_H, was found to have no effect on the velocity of photoreductions.

Effect of p_H on the Velocity of Photoreductions.

Table I.

Molybdate=0·05*M*. *d* (thickness of the cell) = 0·5 cm. I_{abs}=Intensity of energy (366$\mu\mu$) absorbed in ergs per sq. cm. per sec.

(*a*) Glucose = 10% Temp. = 31° I_{abs} = 725		(*b*) Leucine = 1% Temp = 29·5° I_{abs} = 3150		(*c*) Glutamic acid = 1% Temp = 29·5 I_{abs} = 4275		(*d*) α Alanine = 1% Temp = 29·5° I_{abs} = 3420	
p_H.	$K_0 \times 10^{10}$.	p_H.	$K_0 \times 10^{10}$	p_H.	$K_0 \times 10^{10}$.	p_H	$K_0 \times 10^{10}$.
1·35	3·45	0·096	3·17	1·6	1·92	1·81	1·30
2·03	3·58	1·16	3·58	1·81	2·33	2·21	2·08
2·68	3·75	1·57	5·67	2·12	3·00	2·60	2·53
3·66	3·72	1·79	7·20	2·41	3·17	3·20	2·69
4·88	3·67	2·45	8·33	3·50	3·33	4·05	2·42
5·28	3·58	3·33	8·00	4·60	2·83	4·8	2·17
5·75	1·17	4·65	7·83	5·25	2·08	5·4	1·27
		5·30	7·00	5·6	1·18		
		5·48	5·25				
		5·65	4·00				

TABLE II.

d = 0·5 cm. Molybdate = 0·05M. Sodium hypophosphite = 0·083M. Temp. = 29·5°. $I_{abs.}$ = 1696.

A. p_H.	$K_{total} \times 10^{10}$. (light and dark)	$K_{dark} \times 10^{10}$. (K_d)	$K_{light} \times 10^{10}$. [($K_t - K_d$) $\times 10^{10}$]	Conc. of undissociated hypophosphorous acid.
1·63	12·08	4·67	7·42	0·0235 M
1·81	8·75	3·50	5·25	0·019
2·10	6·33	1·83	4·50	0·011
3·01	4·07	0·57	3·57	0·0018
3·94	3·43	...	3·43	0·0005
4·7	3·33	...	3·33	...
5·3	3·08	...	3·08	...
5·6	1·85	...	1·85	

B.

p_H ...	...	1·67	1·81	1·95	2·25	2·70	3·2	4·5
$K_{total} \times 10^{10}$ (light and dark)	...	11·80	8·75	7·00	5·67	3·85	2·18	1·02

The data in group A have been obtained by varying the p_H by addition of caustic soda after the sol has been fully formed by the previous addition of excess of hydrochloric acid, while those in group B have been obtained with the sol prepared by adding just sufficient hydrochloric acid to the molybdate to reach a particular value of p_H. The results in group A indicate an almost constant reaction rate from p_H 2·5 to p_H 5, while those in group B indicate a steady fall with increase in p_H.

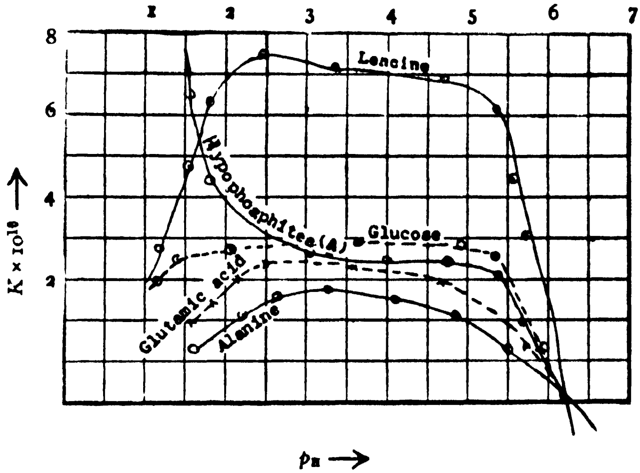
DISCUSSION.

The influence of p_H upon the velocity of photoreductions of molybdic acid sol with glucose and amino-acids is different from that with sodium hypophosphite. We shall treat the two cases separately.

Observations with Glucose and Amino-acids.

The curves in Fig. 1 when produced cut the p_H axis at p_H 6·1 where the velocity of the process is expected to be nil. As the p_H decreases below 6·1, the velocity of reduction rapidly increases, the curves showing a break at p_H 4·7. The velocity of reaction increases slightly with decrease in p_H and a maximum is reached at p_H about 2·5, below which the velocity decreases very slightly.

FIG. 1.



These results are in complete agreement with the conclusions of Jander and others (*Z. anorg. Chem.*, 1930, **194**, 413) who found that different types of molybdic acid micelles are formed at different p_H when H^+ ions are added to an alkali molybdate.

They found that

Above p_H 6·1, the ion has the composition $(MO_4)''$.
At p_H 6·1 the micelle ion $(HMo_3O_{11})'''$ begins to be formed.
At p_H 4·5 the micelle ion $(HMo_6O_{21})'''''$ begins to be formed.
Below p_H 2·9 the micelle ion $(H_3Mo_6O_{21})'''$, $(HMo_{12}O_{41})'''$.
$(H_7Mo_{24}O_{78})'''''$ etc. are formed.

From our observations (*vide* Table I A; also curve with glucose, Fig. 1) on the influence of p_H upon velocity of photoreduction of molybdic acid micelle with glucose, we have seen that up to p_H 6·1, there was no reaction at all as only the ion Mo_4'' exists in true solution.

From our results we can rightly come to the conclusion that as the p_H is lowered below 6·1, photosensitive micelle ion $(HMo_3O_{11})'''$ begins to be formed. This is complete at p_H 4·7. Beyond p_H 4·7, the micelle ion $(HMo_6O_{22})'''''$ which is more photo-active than $(HMo_3O_{11})'''$ commences to grow and this formation is completed at p_H 2·9. Below p_H 2·9, the photo-active micelle ions $(H_3Mo_6O_{21})'''$, $(HMo_{12}O_{41})I'''$, $(H_7Mo_{24}O_{78})'''''$ begins to appear in the system. This is why we observe a maximum in the neighbourhood of p_H 2·9 and slight decrease in velocity with further decrease in p_H.

Observations with Hypophosphite.

The results obtained with hypophosphite are somewhat different from those obtained with glucose and amino-acids. From Table II (*a*) it is evident that dark reaction is proportional to the concentration of undissociated hypophosphorous acid and it disappears when the concentration of undissociated hypophosphorous acid is nil. In other words, the velocity of dark reaction is given by the equation,

$$\left[\frac{dx}{dt}\right]_{\text{dark}} = K \text{ (surface conc. of undissociated hypophosphorous acid)}$$

The light reaction is, however, given by the equation $dx/dt = K_D$ (C_s dissociated reductant) + K_U (C_s, undissociated reductant), C_s denoting surface concentration.

The values of K_D & K_U have been calculated to be $40{\cdot}8 \times 10^{-10}$ and 140×10^{-10} respectively. Table III shows the validity of the equation.

TABLE III.

p_H.	Conc. of hypophosphite		$K_{\text{obs.}} \times 10^{10}$	$K_{\text{calc.}} \times 10^{10}$.
	Dissociated.	Undissociated.		
1·81	0·06 *M*	0·019 *M*	5·25	5·11
2·1	0·072	0·011	4·50	4·48
3·01	0·081	0·0018	3·57	3·56
3·94	0·0825	0·0005	3·43	3·44
4·7	0·083	—	3·33	3·33

Above p_H 4·7, the entire amount of sodium hypophosphite becomes dissociated, and we have only hypophosphite ions in solution. Hence after p_H 4·7, the rate of decrease in velocity with sodium hypophosphite should be comparable with that of glucose, as has been experimentally found to be the case (*vide*, Table IV).

TABLE IV.

p_H.	$K_{\text{hypophosphite}}$.	K_{glucose}.	$\dfrac{K_{\text{hypophosphite}}}{K_{\text{glucose}}}$
4·7	$3{\cdot}33 \times 10^{-10}$	$3{\cdot}7 \times 10^{-10}$	0·90
5·3	$3{\cdot}08 \times 10^{-10}$	$3{\cdot}3 \times 10^{-10}$	0·93
5·6	$1{\cdot}87 \times 10^{-10}$	$2{\cdot}1 \times 10^{-10}$	0·90

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PHOTOCHEMICAL REACTIONS WITH SOME INORGANIC COLLOIDS AS ACTIVE AGENTS UNDER THE INFLUENCE OF LIGHT IN VARIOUS STATES OF POLARISATION PART VI. PHOTOCHEMICAL REDUCTION OF VANADIC ACID SOL WITH ETHYL ALCOHOL IN ACID MEDIUM.

By J. C. Ghosh, T. Banerjee and S. K. Bhattacharjee.

Merck's extra pure ethyl alcohol, sodium meta-vanadate and hydrochloric acid were used in this investigation The vanadic acid sol was prepared every day immediately before each experiment by adding to a solution of sodium meta-vanadate a little greater than half the equivalent amount of hydrochloric acid when a reddish yellow sol was produced.

$$4NaVO_3 + 2HCl = Na_2O, 2V_2O_5 + 2NaCl + H_2O$$

Dumanski (*Kolloid Z.*, 1923, **33**, 147) postulates that by the addition of hydrochloric acid to salts of ortho-vanadic acid, the following changes occur.

$$VO_4''' \rightarrow V_3O_9''' \rightarrow HV_6O_{17}''' \rightarrow V_2O_5 \rightarrow [HV_6O_{17}, nV_2O_5]'''$$

(Colloid particle).

Lange (*Kolloid Z.*, 1932, **59**, 168) determined the relative concentrations of true solutions and colloidal solutions of V_2O_5 by optical methods and his results are given below.

Total conc.	Conc. of colloidal sol.	Conc. of true solution.
14·14*M*	13·53*M*	0·61*M*
7·07	6·26	0·81
2·83	1·64	1·19

In our experiments, the total initial concentration was not less than 8·2 m.*M*. per litre.

The p_H value of the sol was determined electrometrically using quinhydrone electrode which was found to be satisfactory when an accuracy of $\pm 0·2$ in p_H was aimed at.

Spectrophotometric method was applied for the estimation of the reduced vanadic acid sol. Dumanski (*loc. cit.*) found that when V_2O_5 sol is reduced by hydrazine hydrate, the products exist in the colloidal state and exhibits all the properties of colloidal solutions. For our purpose, a König-Marten spectrophotometer was first calibrated. The absorption due to reduced greenish blue vanadic acid sol was measured by means of the spectrophotometer in the red region (632 $\mu\mu$), where the absorption due to original vanadic acid sol is practically negligible. Different concentrations of the vanadic acid sol and the corresponding spectrophotometer readings (θ_2) after complete reduction of the sol by alcohol on long exposure to sunlight are given in Table I.

TABLE I.

Conc. of V_2O_5 sol.	θ_2.	θ_1 (zero reading of spectrophotometer.)	Log tan θ_2 − log tan θ_1.
123×10^{-4} *M*	79·7	46	0·7398
$82{\cdot}5 \times 10^{-4}$	73·3	46	0·4960
$55{\cdot}0 \times 10^{-4}$	65·3	46	0·3161
$41{\cdot}0 \times 10^{-4}$	59·5	46	0·2158
$27{\cdot}5 \times 10^{-4}$	55·0	46	0·1396
$20{\cdot}6 \times 10^{-4}$	51·5	46	0·0839

On plotting log tan θ_2 − log tan θ_1 against concentration of vanadic acid sol, a straight line was obtained (Fig. 1) indicating that Beer's law is obeyed in the case. It is interesting to note that for vanadic acid sol itself Beer's law is not obeyed (Lange, *loc. cit.*) due to the fact that with change in dilution, the equilibrium between molecules in true solution and colloidal solution is disturbed. In our case, however, the total concentration remains constant. What changes, however, is the ratio of micelles in the oxidised and the reduced state.

FIG. 1.

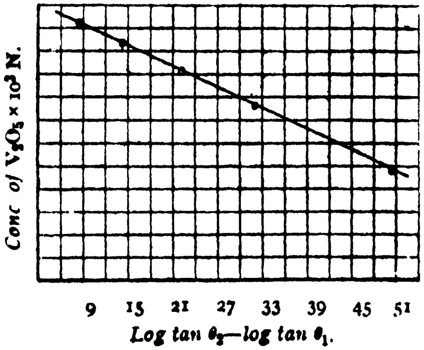
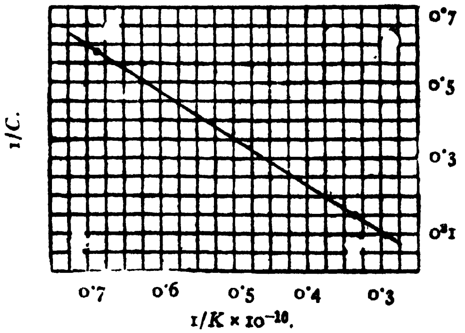


FIG. 2.



From this standard curve (Fig. 1), the concentration of reduced vanadic acid sol at any time after exposure to ultraviolet light was determined by taking the spectrophotometer reading ($\log \tan \theta_2 - \log \tan \theta_1$) corresponding to the absorption in the red region of spectrophotometer.

Dark Reaction.—Vanadic acid sol is not reduced by ethyl alcohol when kept in the dark for a period of 8 hours at 32°.

Determination of the Order of the Reaction.

TABLE II.

Sodium meta-vanadate as $V_2O_5 = 82·5 \times 10^{-4} M$. Alcohol = 10·4 *M*. HCl = 0·01*M*. p_H of the sol = 3·92. Region = 366 $\mu\mu$. Temp. = 32°. $^*I_{abs}$ = 4280.

Time.	Spectro-photometer reading.	V_2O_5 sol × 10^4.	$K_0 \times 10^{10}$ (zero-molecular with respect to V_2O_5 sol) per c.c. per sec.	K (mean).
0 min.	49·5	82·5*M*		
90	54·5	63·7	3·42	
192	63·0	41·5	3·50	3·40
316	69·5	21·0	3·32	

The reaction is evidently zero-molecular.

TABLE III.

Effect of varying the concentration of alcohol.

d = 0·5 cm. I_{abs} = 4280. Temp. = 32°. HCl = 0·01*M*. p_H of sol = 3·9.

V_2O_5 sol × 10^4.	Conc. of alcohol.	$K_0 \times 10^{10}$.	γ.
82·5*M*	10·4*M*	3·4	0·130
,,	6·95	2·98	0·114
,,	3·47	2·43	0·093
,,	1·74	1·47	0·061

On plotting $1/K$ against $1/C$ (ethyl alcohol), a straight line is obtained (Fig. 2).

---

* I_{abs} here and in the following tables indicates the intensity of radiation absorbed in ergs /cm²/ sec. and *d*, the thickness of reaction cell.

TABLE IV.

Effect of varying the concentration of the sol.

$d = 0.5$ cm. $I_{abs} = 4280$ ergs. p_H of the sol $= 3.92$. Temp. $= 32°$.

Conc. of V_2O_5 sol.	Conc. of alcohol.	$K_0 \times 10^{10}$.	γ.
120.0×10^{-4} *M*	6.95 *M*	3.22	0.119
82.5×10^{-4}	,,	2.98	0.112

In the above cases, the p_H value of the sol was kept constant by trial, by adding, where necessary, the requisite quantity of free hydrochloric acid.

The velocity constant, as is evident from Table IV, is independent of the concentration of vanadic acid sol, when the intensity of absorbed radiation is the same.

TABLE V.

Effect of varying the p_H of the system.

Temp. $= 32°$. $I_{abs} = 4280$. V_2O_5 sol. $= 82.5 \times 10^{-4} M$. Alcohol $= 10.4 M$

p_H	...	5.0	3.92	3.31	3.10
$K_0 \times 10^{10}$	...	4.12	3.40	2.17	1.55

Temperature Coefficient of the Reaction.—The temperature coefficient $\left(\frac{K_{T+10}}{K_T}\right)$ is small, being of the order of 1.1.

Effect of Varying the Intensity of Absorbed Radiation.

TABLE VI.

Temperature of the thermostat $= 32°$. Conc. of V_2O_5 sol $= 82.5 \times 10^{-4} M$ p_H of the sol $= 3.92$. Conc. of alcohol $= 10.4 M$.

I_{abs}	...	4280	3249	2085	1299	654
$K_0 \times 10^{10}$	...	3.40	2.77	1.98	1.48	0.92

The velocity constant is proportional neither to the intensity of absorbed radiation nor to the square root of the intensity.

Quantum Efficiency of the Process.—The quantum yield of the photo-process is much less than unity.

A typical calculation is given below :—

We shall take, for example, the reaction in Table II.

The no. of Einstein ($366\mu\mu$) absorbed per sec. per sq. cm.

$$= \frac{4280 \times 366 \times 10^{-7}}{(6{\cdot}55 \times 10^{-27}) \times (3 \times 10^{10}) \times (6{\cdot}1 \times 10^{23})} = 13{\cdot}07 \times 10^{-10}, \quad d = 0{\cdot}5 \text{ cm.,}$$

No. of g. mol transformed in 1 sec. in a cell (1 cm × 1 cm × ·5 cm.)

$$= K_0 \times {\cdot}5 = 3{\cdot}4 \times 10^{-10} \times 0{\cdot}5 = 1{\cdot}7 \times 10^{-10}.$$

$$\gamma \text{ (Quantum efficiency)} = \frac{1{\cdot}7 \times 10^{-10}}{13{\cdot}07 \times 10^{-10}} = 0{\cdot}130.$$

Effect of Polarised Light.

TABLE VII.

$p_H = 5{\cdot}0$

$V_2O_5 = 82{\cdot}5 \times 10^{-4}$ M. Alcohol $= 10{\cdot}4M$

Nature of light		I_{abs}	$M_5 \times 10^{10}$.
Unpolarised	...	654	0·92
l-Circularly polarised light	...	560	0·90
d-Circularly polarised light	...	560	0·58

We see from Table VII that *l*-circularly polarised light is more efficient than *d*-circularly polarised light.

DISCUSSION.

The reaction has the following characteristics :—

(*a*) The velocity of reaction with reference to V_2O_5 sol is zero-molecular.

(*b*) The velocity constant diminishes as the concentration of ethyl alcohol diminishes, the concentration of vanadic acid sol being kept constant. $1/K$ plotted against $1/C_{\text{alcohol}}$ gives a straight line.

(*c*) The velocity constant is almost independent of the concentration of vanadic acid sol, the p_H value being kept constant.

(*d*) The temperature coefficient of the reaction is almost unity.

(*e*) The velocity constant is proportional neither to the intensity of radiation nor to the square root of intensity.

(*f*) The quantum efficiency is much less than unity.

(*g*) *l*-Circularly polarised light is more effective than *d*-circularly polarised light in bringing about the photoreduction of vanadic acid sol with alcohol.

The peculiar feature of the reaction is that the velocity constant is neither proportional to the intensity of radiation nor to the square root of intensity. This indicates that absorption of a quantum of radiation $366\mu\mu$ may

(1) excite a V_2O_5 molecule fixed on the surface of the sol, which reacts with alcohol or

(2) dissociate a V_2O_5 molecule into $V_2O_4 + O$, the molecule of V_2O_4 and oxygen atom reacting separately with alcohol.

For reaction (1)

$$\frac{dx_1}{dt} = \frac{1}{Nh\nu} \cdot KC_s \qquad \ldots \quad (i)$$

(C_s = surface concentration of alcohol)

For reaction (2), since the quantum efficiency is very much less than unity, the surface concentrations of oxygen atom and of V_2O_4 molecule are practically determined by the equation

$$\frac{-}{Nh\nu} \quad \rightarrow V_2O - O$$

$$V_2O_4 + O \rightarrow V\ O_5 \qquad \text{..} \quad (iii)$$

If the rate of the following reactions taking place on the surface of the micelle are approximately the same

$$\left.\begin{array}{l} V_2O_4 + C_2H_5OH \rightarrow V_2O_3 + \text{acetaldehyde} + \text{water} \\ O + C_2H_5OH \rightarrow \text{acetaldehyde} + \text{water} \end{array}\right\} \quad \ldots \quad (iv)$$

the concentration of O atom and V_2O_4 molecule throughout the process are the same, hence

$$[O] = K_3 \sqrt{\frac{1}{Nh\nu}}$$

$$\text{or } [V_2O_4] = K_3 \sqrt{\frac{1}{Nh\nu}}.$$

The velocity of reactions (3) is given by

$$\frac{dx_2}{dt} = K_3 \sqrt{\frac{1}{Nh\nu}} \,.\, K_2 C_s$$

and the total velocity

$$K_0 = \frac{dx}{dt} = \left| \frac{dx_1}{dt} + \frac{dx_2}{dt} \right. = \left[\frac{1}{Nh\nu} + 2K_3 \sqrt{\frac{1}{Nh\nu}} \right] . K . C_s .$$

The rate of oxidation of alcohol also depends on the surface concentration of alcohol. Hence K_0 (the velocity constant of the reactions) will vary as C_s.

But since C_s is given by

$$\frac{K_4 C_{\text{alcohol}}}{K_5 + K_6 C_{\text{alcohol}}} \quad \text{(according to Langmuir's hypothesis)}$$

$1/K_0$ plotted against $1/C_{alcohol}$ should be a straight line, which has actually been found.

The relatively lower efficiency of the *d*-circularly polarised light will be discussed elsewhere in this series.

The effect of p_H on the velocity of reaction in this case is opposite to that observed in the case of tungstic acid and molybdic acid sol. The velocity diminishes with decrease of p_H until we reach p_H, 3 when the sol becomes unstable. This can be best explained on the basis that there is equilibrium in the solution between the following forms

$$[H\,V_6O_{17} + n\,V_2O_5]''' + H^+ \rightleftharpoons [H_2V_6O_{17}\,,\,n\,V_2O_5]''$$

$$[H_2V_6O_{17},\,n\,V_2O_5]'' + H^+ \rightleftharpoons [H_3V_6O_{17}\,,\,n\,V_2O_5]',$$

and so on.

With increase in the concentration of H′, the negative charge on the colloid micelle diminishes, and with diminution in the density of charge, particles become larger and larger. Hence the specific surface diminishes which results in a diminution in the velocity of the surface reaction which we have studied.

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PHOTOCHEMICAL REDUCTIONS WITH SOME INORGANIC COLLOIDS AS ACTIVE AGENTS UNDER THE INFLUENCE OF LIGHT IN VARIOUS STATES OF POLARISATION.

PART VII. PHOTOCHEMICAL REDUCTION OF URANIC ACID SOL BY SODIUM TARTRATE.

By J. C. Ghosh, T. Banerjee and J. C. Bose.

In this part the characteristic features of uranic acid sol as a photochemical oxidant have been described.

EXPERIMENTAL.

Preparation of Uranic Acid Sol.—A clear golden yellow coloured sol was obtained according to the method of Szilard (*J. chim. phys.*, 1907, **5**, 488, 636).

Estimation of Uranic Acid Sol prepared.—The uranium content of the sol was estimated as U_3O_8 (Treadwell and Hall, "Analytical Chemistry" 1924, Part II, p 107).

Experimental Procedure.—No reduction was observed on exposing solution of uranic acid sol alone to ultraviolet rays (366 $\mu\mu$ and 336 $\mu\mu$).

The photoreduction in presence of sodium tartrate has been estimated by titrating potentiometrically with a solution of potassium dichromate (Ewing and Eldridge *J. Amer. Chem. Soc.*, 1922, **44**, 1484). When a solution of potassium dichromate is gradually added to uranous salt, the E. M. F. of the system, measured against a calomel electrode, increases and at the null point (*i.e.*, when all the uranous salt has been converted into uranyl), a sudden rise of E. M. F. takes place under suitable experimental conditions.

As the uranous salt is very easily oxidised by the oxygen of the atmosphere, a layer of liquid paraffin was spread over it; and more over, the titrations were done in an atmosphere of carbon dioxide.

Several blank determinations of uranous salt in this laboratary by the potentiometric method gave results which were concordant within ±0·2%. The results were further confirmed by the titration of the uranous salt with standard potassium permanganate solution.

Merck's chemically pure sodium tartrate was twice crystallised from water.

It was found that uranic acid sol does not react with sodium tartrate when kept in the dark for 10 hours.

In the following tables, d denotes the thickness of the reaction cell, I_{ab}., the intensity of radiation absorbed in ergs per sq. cm. and γ=quantum efficiency.

RESULTS.

Effect of Varying the Concentration of Uranic Acid Sol.

TABLE. I.

d = 0·5 cm. Conc. of uranic acid sol=0·017M. Temp., 30°. Sodium tartrate=0·333M. I_{abs} = 2170. Dichromate=0·01N

Time.	C.c. of dichromate ≡ ·252 c.c. reaction mixture.	$K = 2{\cdot}3 \times \frac{a}{t_{sec}} \times \log\frac{a}{a-x}$.
0	0·0	
120	0·35	$1{\cdot}23 \times 10^{-6}$
360	0·68	$1{\cdot}23 \times 10^{-6}$
600	0·79	$1{\cdot}11 \times 10^{-6}$
		Mean $1{\cdot}19 \times 10^{-6}$

Similar readings were taken with other concentrations of uranic acid sol and the results are given below.

Sodium tartrate.	Uranic acid sol.	$K = 2{\cdot}3 \times \frac{a}{t_{sec}} \log\frac{a}{a-x}$ (1)	γ.
0·333M	0·026M	$1{\cdot}07 \times 10^{-6}$	0·70
,,	0·017	$1{\cdot}19 \times 10^{-6}$	0·72
,,	0·013	$1{\cdot}15 \times 10^{-6}$	0·68

Effect of Varying the Concentration of Sodium Tartrate.

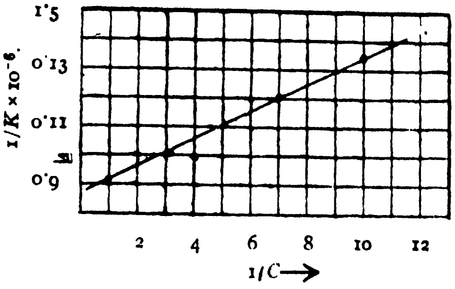
TABLE II.

Temp.=30°. I_{abs} =2170 ergs.

Sodium tartrate	Uranic acid sol.	K (1).	γ.
0·333M	0·026M	$1{\cdot}07 \times 10^{-6}$	0·70
0·166	,,	$0{\cdot}91 \times 10^{-6}$	0·60
0·083	,,	$0{\cdot}73 \times 10^{-6}$	0·55

It is found that $1/K$ plotted against $1/C_{tartrate}$ gives approximately a straight line. (Fig 1).

FIG. 1.



Effect of Varying the Temperature.—Temperature coefficient $\left(\frac{K^{40^\circ}}{K^{30^\circ}}\right)$ is small being of the order of 1·1—1·2.

Effect of Varying the Intensity of Radiation Absorbed.

TABLE III.

I_{abs}.	Uranic acid sol.	Sodium tartrate.	K(1).
2170	0·026M	0·166M	$0·91 \times 10^{-6}$
530	,,	,,	$0·23 \times 10^{-6}$
2170	,,	0·083	$0·730 \times 10^{-6}$
530	,,	,,	$0·18 \times 10^{-6}$

It will be seen from the above table that the velocity constants vary directly as the intensity of radiation absorbed.

Quantum Efficiency of the Process.—Quantum efficiency is a litile less than unity, being of the order of 0·55—0·72.

Effect of Polarised Light on the Reduction.

TABLE IV.

Nature of light.	Intensity of I_{abs}.	Uranic acid	Sodium tartrate.	K(1).
Unpolarised	2170	0·017M	0·333M	$1·19 \times 10^{-6}$
***d*-Circularly polarised**	300	,,	,,	$0·165 \times 10^{-6}$
***l*-Circularly polarised**	300	,,	,,	$0·157 \times 10^{-6}$

The above table shows that on the assumption that the velocity constant varies directly as the intensity of radiation absorbed

$$V_O = V_L = V_D ,$$

V_O , V_L , V_D having the same significance as in Part II.

DISCUSSION.

It will be seen from the previous tables that the velocity constants are concordant when given by the equation

$$\frac{a}{t} \log \frac{a}{a-x} \qquad \ldots \quad (i)$$

This equation is obviously the integral of

$$\frac{dx}{dt} = K \frac{a-x}{a} .$$

During the process of photochemical reduction of uranic acid sol, uranous acid is formed. The active radiation is absorbed both by uranic acid and the resulting product uranous acid. It has been found experimentally that almost the whole of the incident radiation is absorbed by the reaction mixture; variation of the composition of the reaction mixture within considerable range does not affect this property. The molecular extinction coefficients of uranic acid and uranous acid in the near ultraviolet is of the same order and if "I" is the intensity of radiation absorbed by the reaction mixture, we may assume that the fraction absorbed by uranic acid is $\frac{a-\lambda}{a} \times I$, and that by uranous acid is $\frac{\lambda}{a} I$. Now it is the fraction of light that is absorbed by uranic acid which is photochemically active; and hence the number of excited molecules of uranic acid produced per sec.

$$= K(a-x/a) \times I/Nh\nu.$$

If C_s is the surface concentration of the tartrate on the micelle

$$\frac{dx}{dt} = K \frac{(a-x)}{a} . \frac{I}{Nh\nu} . C_s$$

But following Langmuir's hypothesis, we have

$C_s = \frac{K_1 C_t}{1+K_2 C_t}$ where C_t is the bulk concentration of the tartrate in the solution.

$$\therefore \frac{dx}{dt} = K\frac{(a-x)}{a} \frac{I}{Nh\nu} \cdot \frac{K_1 C_t}{1+K_2 C_t}$$

For excess tartrate concentration, and constant intensiiy of radiation,

$$K = \frac{a}{t} \log \frac{a}{a-x}.$$

which has been found to be case. Again K should be proportional to light intensity "I" which has also been found to be the case, the quantum efficiency being of the order of unity.

K also is proportional to $\frac{K_1 C_t}{1+K_2 C_t}$

or $\frac{1}{K}$ is proportional to $\frac{K_2}{K_1} + \frac{1}{K_1 C_t}$ or $\frac{1}{K}$ plotted against $\frac{1}{C_t}$ should give a straight line, which has also been found to hold good.

It will be noticed that unlike the sol tungstic acid and vanadic acid, which have greater photochemical efficiency when excited by *l*-circularly polarised light than by *d*-circularly polarised light, the photochemical efficiency of uranic acid sol when excited by equal intensities of both types of circulárly polarised light is the same.

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ENZYMES IN SNAKE-VENOM. PART III. EFFECT OF TEMPERATURE AND CHEMICALS ON THEIR ACTIVITY.

By M. L. Kundu, S. S. De and B. N. Ghosh.

In two papers published previously (Ghosh, *J. Indian Chem. Soc.*, 1936, **13**, 450; Ghosh and De, *ibid.*, 1936, **13** 627) it has been shown that the venoms of cobra (*Naja Naja*) and of Daboa (*vipera Russelli*) contain proteolytic enzymes, the optimum activity of which is in the neighbourhood of p_H 7·0 when casein is used as substrate and at p_H 8·0 to 8·2 when gelatin and egg-albumin are used instead of casein. It has also been shown that these venoms can oxidise hæmoglobin to methæmoglobin and can hydrolyse Witte's peptone; the optimum p_H for the latter reaction being 8·2 to 8·4. Further work on this line was carried out with the venoms of Krait (*Bungarus fasciatus*) and of *Echis carinata*. The effect of temperature and of chemicals like potassium cyanide on the activity of the proteolytic enzymes present in the venoms of cobra, Daboa, and *Echis carinata* were also investigated. The results obtained are recorded in this paper.

EXPERIMENTAL.

Action of Venoms of Krait and of Echis carinata on Proteins.

The experimental procedure adopted was similar to that described by Ghosh (*loc. cit.*) in a previous paper. Stock solutions (5%) of gelatin, Merk's dried egg-albumin and of casein were prepared and kept in a refrigerator with a few drops of toluene as preservative.

Solutions of venoms of Krait (*Bungarus fasciatus*) and of *Echis carinata* in 0·9% NaCl were prepared and their toxicity determined by intravenus injection into pigeons weighing between 300 and 310 g. It was found that the lethal doses for pigeons, of Krait and of *Echis carinata* venom were 0·4 mg. and 0·055 mg. respectively.

The stock protein solution (20 c.c.) was taken in a conical flask and its reaction adjusted to the requisite value by adding a few drops of HCl or NaOH according to need. To this solution, 10 c.c. of buffer solution of the desired p_H were added. 10 C.c. of this buffered protein solution were placed in each of the two conical flasks. To one of the flasks, 2 c.c. of venom solution and 8 c.c. of 0·9% NaCl solution were added. To the other, which served as control, 10 c.c. of 0·9% NaCl solution only were added. After the addition of a few drops of toluene to each of the flasks, they were stoppered and placed in a thermostat at 37°. At suitable intervals of time, 5 c.c. portions of the solution were withdrawn from each set of flasks, and added to 45 c.c. of absolute alcohol containing 0·5 c.c. of a 0·5% thymolphthalein solution in alcohol. To the flask containing the 5 c.c. control sample, 0·5 c.c. of venom solution was added just before titration. The buffer solutions used were acid potassium phthalate from p_H 2·2 to p_H 5·8, acid potassium phosphate from p_H 6·0 to 8·0 and boric acid and potassium chloride from p_H 8·2 to 10·0. The interval of time allowed for digestion after the addition of venom solution and before titration (briefly denoted as *incubation period*) was for Krait venom 14 hours and for *Echis carinata* venom 6 hours.

TABLE I.

Substrate—Egg-albumin. Venom—*Echis carinata.*

0·0366*N*-EtOH-KOH reqd. to titrate 5 c.c. of soln

p_H.	Active venom + substrate.	Control.	Diff.	p_H.	Active venom + substrate.	Control.	Diff.
5·0	3·33 c.c.	3·25 c.c.	0·08 c.c.	7·5	3·16	2·57	0·59
6·0	4·2	3·90	0·30	8·0	2·72	2·10	0·62
6·5	3·81	3·40	0·41	8·6	2·28	1·70	0·58
7·0	3·52	3·00	0·52	9·0	1·85	1·40	0·45
				9·5	1·29	1·01	0·28

TABLE II.

Substrate—Casein. Venom—*Echis carinata.*

0·0366*N*-EtOH-KOH reqd. to titrate 5 c.c. of soln.

p_H.	Active venom + substrate.	Control.	Diff.	p_H.	Active venom + substrate.	Control.	Diff.
5·0	3·81 c.c.	3·60 c.c.	0·21 c.c.	7·5	3·55	2·85	0·70
6·0	5·06	4·62	0·44	8·0	2·77	2·1	0·66
6·6	4·61	4·02	0·59	8·5	2·21	1·65	0·56
7·0	4·06	3·4	0·68	9·0	1·57	1·12	0·45
				9·5	1·13	0·92	0·21

Table III.

Substance—Gelatin. Venom—*Echis carinata.*

0·0366*N*-EtOH-KOH reqd. to titrate 5 c.c. of soln.

p_H.	Active venom + substrate.	Control.	Diff.
5·0	2·08 c.c.	2·01 c.c.	0·07 c.c.
6·0	2·83	2·56	0·27
6·5	2·49	2·11	0·38
7·0	2·38	1·91	0·47
7·6	2·31	1·80	0·51
8·0	1·95	1·41	0·54
8·5	1·72	1·22	0·50
9·0	1·52	1·10	0·42
9·5	1·15	0·90	0·25

Table IV.

Substrate—Casein. Venom—Krait (*Bungarus fasciatus*).

0·0452*N*-EtOH-KOH reqd. to titrate 5 c.c. of soln.

p_H.	Active venom + substrate.	Control.	Diff.
6·0	4·81 c.c.	3·76 c.c.	1·05 c.c.
7·0	4·54	2·78	1·76
7·4	4·18	2·37	1·81
8·0	3·36	1·74	1·62
9·0	1·90	0·98	0·92

Table V.

Substrate—Gelatin. Venom—Krait (*Bungarus fasciatus*).

0·0452*N*-EtOH-KOH reqd. to titrate 5 c.c. of soln.

p_H.	Active venom + substrate.	Control.	Diff.
6·0	2·48 c.c.	2·10 c.c.	0·38 c.c.
7·0	2·23	1·58	0·65
7·6	2·22	1·32	0·90
8·0	2·13	1·15	0·98
9·0	1·61	0·92	0·69

From an examination of data recorded in the Tables I—III, it appears that the optimum activity of the proteolytic enzyme in the venom of *Echis carinata* is at p_H 8·0—8·2, the substrates being gelatin and egg-albumin; when, however, casein is used as substrate its optimum activity is in the neighbourhood of p_H 7·0.

Again it will be noticed from the data in the Tables IV and V that with casein and gelatin as substrates, the optimum activity of the protease in the venom of Krait (*Bungarus fasciatus*) is also in the neighbourhood of p_H 7.0 and p_H 8·0 respectively.

Action of the Venoms of Krait and Echis carinata *on Peptone.*

Although it has been recorded by Launoy (*compt. rend.*, 1902, 135, 401) that the venoms of cobra and of the vipers can hydrolyse the native proteins, leading to the formation of albumose, yet it was not known until recently that these venoms can act on peptone. It has recently been shown by Ghosh and De (*loc. cit.*) that the venoms of cobra (*Naja Naja*) and *vipera Russelli* contain enzymes which can hydrolyse Witte's peptone. In this paper the results obtained with the venoms of Krait and of *Echis carinata* are recorded in the following tables.

TABLE VI.

Substrate—Peptone. Venom—*Echis carinata.* Incubation period—6 hrs.

	0·0366*N*-EtOH-KOH reqd. to titrate 5 c.c. of solution.		
p_H.	Active venom + substrate.	Control.	Diff.
5·0	6·91	6·80 c.c.	0·11 c.c.
6·0	6·56	6·30	0·26
6·5	6·17	5·80	0·37
7·0	5·49	5·00	0·49
7·6	4·49	3·90	0·59
8·0	3·74	3·10	0·64
8·5	3·08	2·45	0·63
9·0	2·44	1·90	0·54
9·5	2·00	1·50	0·50

TABLE VII.

Substrate—Peptone. Venom—Krait. Incubation period—14 hrs.

0·0452*N*-EtOH-KOH reqd. to titrate 5 c.c. of soln.

p_H.	Active venom + substrate.	Control.	Diff.
6·0	5·96 c. c.	5·58 c.c.	0·38
6.6	5·14	4·70	0·44
7·0	4·64	4·10	0·54
7·6	3·80	3·15	0·65
8·0	3·25	2·56	0·69
8·5	2·62	1·92	0·70
9·0	2·20	1·54	0·66

It will be noticed from the data recorded in the Tables VI and VII that the enzyme contained in the venoms of both the snakes can hydrolyse Witte's peptone and that its optimum activity lies between p_H 8·2 and p_H 8·4.

Effect of Temperature on the Activity of the Protease in Snake-venom.

A rise in temperature affects enzyme reactions in two ways, *viz.*, (*i*) it increases the velocity of reaction, and (*ii*) it begins to destroy the enzyme at higher temperatures. As a result of these two opposing factors acting simultaneously, the velocity of an enzyme reaction will at first increase, reach a maximum and then decrease as the temperature is raised. Investigations were made to determine the temperature at which the velocity of hydrolysis, caused by the proteolytic enzymes present in the venoms of cobra, Russell's viper and *Echis carinata* is the maximum. The experimental procedure was the same as described already. The data obtained at p_H 7·6 are plotted in Fig. 1. The substrate used in these experiments was casein. The results obtained by using 1 mg. of Merck's trypsin are also recorded below for the purpose of comparison. The amount of venom used per 20 c.c. of the substrate solution was 60 mg. for cobra and Russell's viper and 10 mg. for *Echis carinata.*

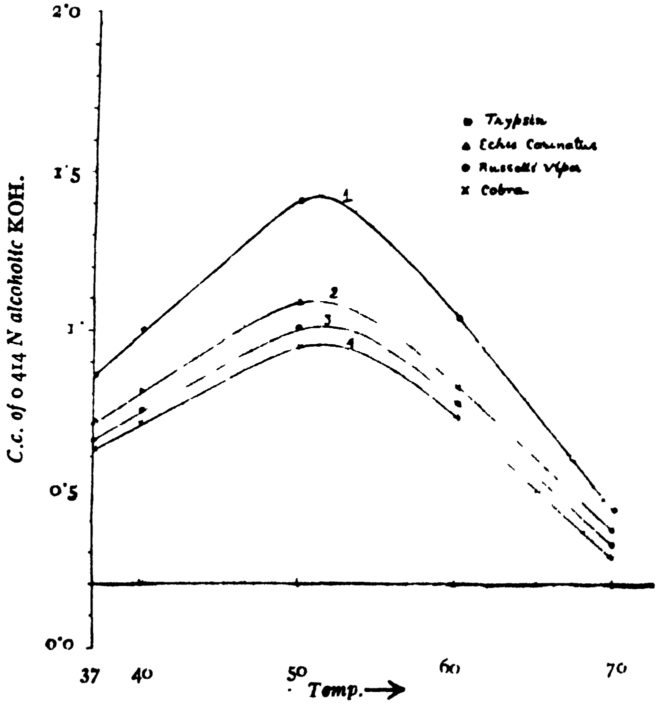
TABLE VIII.

Incubation period—6 hrs.

Source of enzyme taken.	p_H.	Control.	0·0414*N*-KOH reqd. to titrate 5 c.c. of the soln. 37°.	40°.	50°.	60°.	70°.
Cobra venom	6·6	3·76 c.c.	4·24 c.c.	4·32 c.c.	4·49 c.c.	4·34 c.c.	3·92 c.c.
	7·6	2·70	3·32	3·40	3·65	3·42	2·98
	8·6	1·56	1·93	1·98	2·11	2·01	1·74
Russell's viper venom	6·6	3·62	4·22	4·30	4·55	4·32	3·86
	7·6	2·64	3·29	3·38	3·65	3·40	2·96
	8·6	1·55	1·91	2·00	2·27	2·03	1·75
Echis carinata venom	6·6	3·54	4·08	4·17	4·42	4·19	3·76
	7·6	2·55	3·25	3·35	3·63	3·37	2·90
	8·6	1·47	1·80	1·88	2·15	1·91	1·65
Trypsin	6·6	3·51	4·16	4·29	4·63	4·25	3·81
	7·6	2·50	3·36	3·50	3·91	3·55	2·92
	8·6	1·42	2·03	2·16	2·46	2·10	2·66

It will be noticed from Fig. 1 and from the data recorded in Table VIII that the maximum activity of the protease present in the venoms of cobra, Russell's viper and *Echis carinata* is in the neighbourhood of 50°. This is also the temperature at which the rate of hydrolysis of casein by trypsin (Merck's) is the maximum.

FIG. 1.



Curves 1-4 refer respectively to trypsin, *Echis carinata*, Russell's viper and cobra.

The Effect of Poisonous Chemicals on the Activity of the Protease in Snake-venom.

It is a known fact that poisonous substances like KCN influence the activity of the proteolytic enzymes favourably or unfavourably, depending on the nature of the enzyme. Experiments were, therefore, carried out to determine the effect of compounds like KCN, $HgCl_2$ and H_2S on the activity of the proteolytic enzymes present in the venoms of cobra, Russell's viper, and *Echis carinata.* The results obtained at p_H 7·6 only, are recorded ; the inhibition observed at p_H 6·6 and at 8·6 being of the same order of magnitude as at p_H 7·6.

TABLE IX.

Effect of Potassium Cyanide.

Incubation period – 16 hrs. p_H of the substrate – 7·6.

	0·0448 *N*-EtOH-KOH reqd to titrate 5 c.c. of soln.				
	(I)	(II)	(III)	(IV)	(V)
				Inhibition	
Venom used	Venom only.	Venom + KCN (0·00036*M*).	Venom + KCN (0·00072*M*).	Diff. bet. I & II.	Diff. bet. I & III.
Cobra	3·09 c.c.	3·07 c.c.	2·81 c.c.	0·02 c.c.	0·28 c.c.
Russell's viper	3·06	3·06	2·81	0·00	0·25
Echis carinatus	2·91	2·89	2·66	0·02	0·25
Trypsin	3·10	3·12	2·81	0·02	0·29

TABLE X.

Effect of Hydrogen Sulphide.

EtOH-KOH (0·0493 *N*) reqd. to titrate 5 c.c. of soln.

	(I)	(II)	(III)	(IV)	(V)
				Inhibition	
Venom used.	Venom only.	Venom + H_2S (0·00018 *M*).	Venom + H_2S (0·00054*M*).	Diff. bet. I & II.	Diff. bet. I & III.
Cobra	2·92 c.c.	2·90 c.c.	2·54 c.c.	0·02 c.c.	0·38 c.c.
Russell's viper	2·77	2·76	2·47	0·01	0·30
Echis carinatus	2·65	2·65	2·37	0·00	0·28
Trypsin	2·84	2·83	2·46	0·01	0·38

TABLE XI.

Effect of Mercuric Chloride.

EtOH-KOH (0·0407 *N*) reqd. to titrate 5 c.c. of soln.

Venom used.	(I)	(II)	(III)	(IV)	(V)
	Venom only.	Venom + $HgCl_2$ (0·00065*M*).	Venom + $HgCl_2$ (0·0013*M*).	Inhibition Diff. bet. I & II.	Diff. bet. I & III.
Cobra	3·42 c.c.	3·41 c.c.	3·19 c.c.	0·01 c.c	0·23 c.c.
Russell's viper	3·39	3·38	3·20	0·01	0·19
Echis carinatus	3·20	3·19	3·04	0·01	0·16
Trypsin	3·41	3·40	3·21	0·01	0·20

It will be seen from the above data that the three compounds KCN, $HgCl_2$ and H_2S inhibit the activity of the protease present in the venoms of the snakes mentioned already. These poisonous compounds at the concentrations at which they have been used also inhibit the action of trypsin.

SUMMARY.

1. Using casein as substrate, the optimum activity of the protease in the venoms of *Echis carinata* and Krait is in the neigbourhood of p_H 7·0. When gelatin or egg-albumin is used instead of casein, the optimum activity of the protease lies between p_H 8·0—p_H 8·2.

2. The venoms of Krait and *Echis carinata* can hydrolyse peptone and the optimum activity of the enzyme lies between p_H 8·2—8·4.

3. The maximum rate of hydrolysis of casein by trypsin and by the protease present in the venoms of cobra, Russell's viper and *Echis carinata* occurs in the neighbourhood of 50°.

4. Compounds like KCN, $HgCl_2$ and H_2S inhibit the activity of trypsin and of the protease present in the venoms of cobra, Russell's viper and *Echis carinata*.

Our best thanks are due to the Director of the Central Research Institute, Kasauli for his kind gift of the Krait venom and to the authorities of the Bengal Immunity for a research grant.

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A NOTE ON THE TWO DIFFERENT MODIFICATIONS OF COBALT QUINALDINATE.

BY NIHAR KUMAR DUTT.

Quinaldinic acid has been introduced by Rây and Bose (*Z. anal. Chem*, 1933, **95**, 400) as a reagent for the estimation of Cu, *Zn*, Cd and U, and for their separation from various other elements and radicals. The authors have also described (*loc. cit.*) a number of metallic salts of the acid, and the occurrence of two different modifications of the ferrous quinaldinate (*cis-* and *trans-* form) has been accounted for. It has now been observed that the cobalt quinaldinate also exists in two different modifications—one cream-coloured and the other rose-red. Though they differ only in the water of hydration, the red variety being anhydrous, it was found interesting to study their mode of formation, conditions of mutual transformation and their characteristic properties.

Mode of Formation.

1. When a neutral solution of any cobalt salt is added to a neutral solution of sodium quinaldinate in the cold, a cream-coloured precipitate is formed ; on boiling, the precipitate becomes granular.

2. When the cobalt salt solution is acidified with a drop or two of acetic acid and then treated with sodium quinaldinate solution in the cold, the cream-coloured precipitate is formed as before ; but on keeping the mixture on the water-bath for some time, the precipitate changes into the rose-red crystalline variety.

3. When a slightly acidified (with acetic acid) hot cobalt salt solution is mixed with a hot solution of sodium quinaldinate, the rose-red precipitate is formed at once.

These facts show that the presence of $H^{\cdot}$ ion coupled with rise of temperature (80–90°) favours the formation of the red variety or the transformation of the cream-coloured product into the latter.

The cream-coloured variety was, however, found to be stable in the dry state even up to a temperature of 160°, above which it lost its water and changed into the red modification.

Magnetically both the substances were paramagnetic, the red variety giving a somewhat smaller susceptibility value.

Cobalt Quinaldinate (*cream*).—The cream-coloured variety was prepared in the cold as described under 2. The precipitate was washed with cold water and dried in *vacuo* over concentrated H_2SO_4 to a constant weight. [Found : N, 6·20 ; Co, 13·47, 13·50. Co $(C_{10}H_6NO_2)_2 . 2H_2O$ requires, N, 6·25; Co, 13·46 per cent].

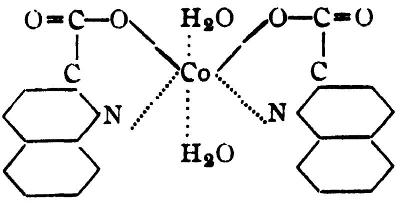
Cobalt Quinaldinate (*red*).—The red anhydrous variety was obtained as described under 3. This was washed with hot water and dried as in the previous case. [Found: N, 6·90 ; Co, 14·60, 14·50. Co $(C_{10}H_6NO_2)_2$ requires N, 6·95 ; Co, 14·61 per cent].

Magnetic Susceptibility.

At 23°.		$\chi_m \times 10^6$.	$\chi_M \times 10^6$.	P_{weiss}.
Cream salt	...	20·19	8863·4	22·82
Red salt	...	19·21	7741·63	21·27

The measurements were made in a Curie's balance. P_{weiss} for Co-atom either as free Co^{++} ion or in complex cobaltous salts (imperfect or associated complexes) has been found to vary between 22—26.

Both the cream and red cobalt quinaldinates are evidently co-ordination compounds of the imperfect or associated type. The co-ordination number for the central cobalt atom in the cream-coloured hydrated compound is **six**, whereas in the rose-red variety it is four only. It may be further assumed from a consideration of the colour of the salts that the two water molecules in the hydrated cream-coloured modification occupy *trans*-positions. These molecules of water cannot be removed below 160° and, therefore, form actually a part of the co-ordination complex.



Cobalt quinaldinate ... cream.

My greatful thanks are due to Mr. P. Rây for his kindly suggesting this piece of work to me.

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PHOTOCHEMICAL REACTION WITH SOME INORGANIC COLLOIDS AS ACTIVE AGENTS UNDER THE INFLUENCE OF LIGHT IN VARIOUS STATES OF POLARISATION. PART VIII. ON THE INTERNAL FILTER ACTION OF REDUCED TUNGSTIC ACID AND MOLYBDIC ACID SOLS.

By Tarapada Banerjee and J. C. Ghosh.

In the previous papers (Parts II, III, IV and V of this series, this Journal, September issue, Vol. XIV) it has been shown that the photoreduction of sols of tungstic acid and molybdic acid by ultraviolet light of wave-length $366\mu\mu$ with glucose, laevulose, etc. as reductants has the following characteristic features:—

(1) The velocity of reaction which was followed up to 30% reduction of the photo-active sol, is proportional to the intensity of light absorbed by the reaction mixture, the quantum efficiency being of the order of $0{\cdot}5 - 1{\cdot}0$.

(2) That with excess of reductant, the reaction follows the zero-molecular law, *i.e.*, equal amount of sol is reduced in equal time independent of the ratio of the oxidised and reduced forms of the sol in the system.

It is necessary to mention that these results are obtained only when sufficient precaution has been taken to exclude oxygen from the reaction mixture; otherwise the reduced sol gets re-oxidised by molecular oxygen and erratic velocity constants (sometimes of a unimolecular type) are obtained.

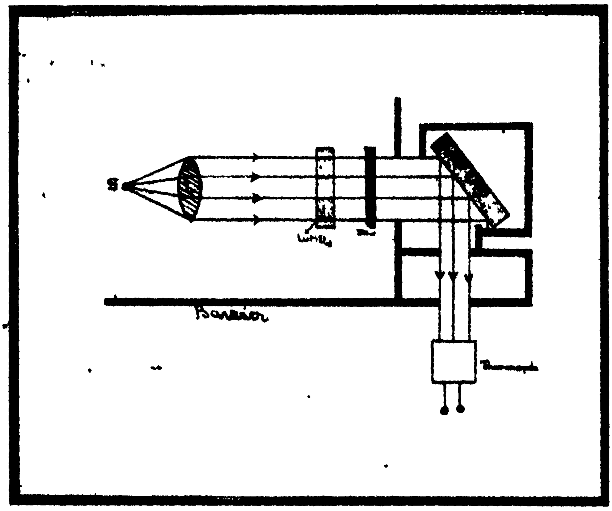
Normally it is to be expected that in such simple systems, the velocity of reaction should be proportional to the light absorbed by the photo-active sol in the higher state of valency, the fraction of the light absorbed by the reduced form of the sol going to waste merely as heat. If the extinction coefficient of the reduced form is of the same order as the original sol, the light absorbed by the photo-active sol will continually become less and less during the progress of the reaction. As a matter of fact, the extinction coefficient of the reduced sol has been found to be much higher than that of the original unreduced sol. A zero-molecular velocity constant is, therefore, contrary to expectation and the problem necessiated a thorough investigation.

As a probable explanation, it was thought that though the reaction mixture did not indicate any turbidity in visible light, the scattering coefficient of the sol for the active ultraviolet radiation may be considerable, and perhaps much larger than that of the reduced sol. With progress in reaction, the loss due to scattering may be less and compensate for the continuously diminishing light absorption by the active sol. The following experiment (*vide* Fig. 1) was carried out to test this possibility.

EXPERIMENTAL.

Light from the source S, a point-o-lite mercury lamp, is rendered parallel by the lens L, passes through the quartz cell containing 2% $CuSO_4$ solution in water and through the ultraviolet filter (glass filter No. G 312, *vide* Technological papers of the Bureau of Standards, No. 148) and falls at an angle of 45° upon the quartz cell containing the solution whose scattering power is to be measured. The reflected light is received by the Moll thermopile connected with a very sensitive Moll galvanometer. It was found that the total amount of light scattered by the quartz surface and the solution is about 3% of the total incident light. If the light falls normally upon C (Fig. 1), it will be still less. When reduced sol was taken in C, the amount of light scattered was even somewhat less than 3%. Any explanation of our experimental observation as due to variation in the scattering coefficient, is therefore, impossible.

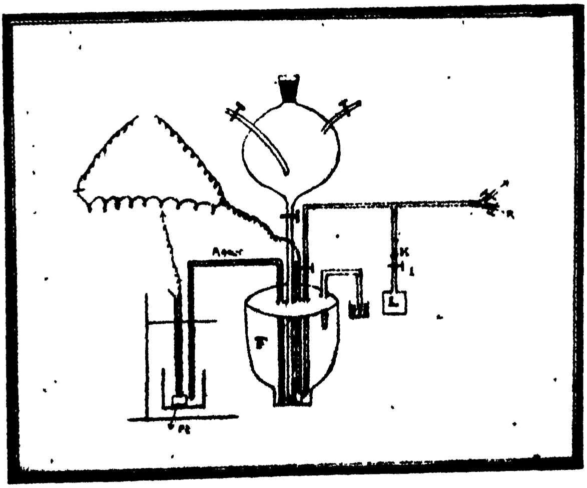
FIG. 1.



The phenomenon of two dimensional mobility discovered by Volmer (Summary given in *Trans. Faraday Soc.*, 1932, **28**, 359) gave a clue to the proper understanding of the problem. The surface of micelles of tungstic acid sol is initially covered with WO_3 molecules. When such molecules absorb radiation, they get activated. The unactivated adsorbed molecules are mostly bound to the fixed atoms of the underlying material and can only oscillate around their equilibrium positions. When it absorbs a quantum of radiation, its amplitude of oscillation increases; and if a sufficient part of the radiant energy absorbed is transformed into kinetic energy, the particles will have considerable surface mobility. Under such conditions it does not matter whether light quantum is absorbed by a tungstic acid molecule or a reduced tungstic acid molecule on the micelle surface. For the activated reduced molecule will give its energy of activation by surface collision to a tungstic acid molecule which in its turn will get reduced by reaction with the reductant.

The critical test of such a hypothesis is possible. If for example, it is possible by suitable experimental methods, to bring every molecule of tungstic acid in a micelle to a lower state of valency, then the light absorbed by such a completely reduced micelle will not be available for photochemical reaction In our photochemical investigation, the micelles of the active sol were not reduced to more than 30% in course of 10 hours; but the complete reduction of a micelle of tungstic acid or molybdic acid can be easily effected either by exposure to sunlight in presence of excess of reductant or by cathodic discharge of hydrogen ions. If such completely reduced sol is now mixed with a reacting system consisting of tungstic acid sol and reductant, taking great care that in the process of mixing, the completely reduced micelles do not get any chance of being partially oxidised by oxygen gas, we would expect that the part of the light

FIG. 2.



radiations absorbed by the completely reduced micelles will not be available for photoreduction. This has been observed to be the case and a direct proof of the two dimensional mobillty of molecules of tungstic acid and molybdic acid on micelle surfaces has thus been obtained.

In Fig. 2 is described the experimental arrangement for the complete cathodic reduction of a sol of tungstic acid, its anaerobic mixing with original sol and reductant and transference of the mixture to the quartz reaction vessel L which is provided with a long neck and a ground glass joint K with a stop-cock I below the joint.

The flask F contains the tungstic acid sol and had five connections with ground glass joints and water-seals.

(*i*) Through a three-way stop-cock to vacuum pump, reaction cell and hydrogen generator.

(*ii*) To H_2 gas outlet tube.

(*iii*) To Pt electrode.

(*iv*) To a separating funnel containing a mixture of tungstic acid sol and reductant closed at the top with a rubber stopper holding internally sealed glass tubes for inlet and outlet of hydrogen.

(*v*) To an agar bridge tube connecting the anode-chamber.

The electrolytic reduction was carried out on a platinum cathode, purified hydrogen gas from a Kipp's apparatus bubbling vigorously through the solution during the electrolysis. When the reduction was completed and the solution cooled to room temperature, the reaction mixture from the separating funnel is poured down under the pressure of H_2 gas above, and thoroughly agitated by the H_2 gas bubbling in F. The mixture was transferred to the reaction vessel with the aid of pump, stop-cock I closed and the vessel taken out from the system by disconnecting the joint at K.

An arrangement similar to the above was also used for complete reduction of the sols in sunlight and subsequent mixing with a definite volume of a mixture of the original sol and reductant and transference to the reaction vessel.

In determining the extinction coefficient, the reduced sol was diluted to the required concentration with air-free redistilled water from the separating funnel.

Measurements of Extinction Coefficient.

TABLE I

d (thickness of the cell) = 0·5 cm. $\lambda = 366\mu\mu$.

	Substance whose extinction coeff is to be measured.	Conc. of the substance used (c)	Transmission of radiation in ergs/cm²/ sec. through		Ext. coeft. $= \dfrac{2\cdot3 \log \frac{I_0}{I_d}}{c.\ d}$
			water in the cell. (I_0)	soln. in the cell. (I_d)	
1.	Tungstic acid sol	0·05M	1070	66·7	111
2.	Completely reduced tungstic acid sol	0·005	1070	396·3	400
3.	Molybdic acid sol	0·05	1373	475·2	43
4.	Do	0·05	884·5	297·0	45
5.	Completely re-reduced molybdic acid sol	0·00268	1373	191·5	1450
6.	Do	0·000667	1373	812·0	1550

TABLE II.

With tungstic acid sol.

Glucose = 2·5%. p_H = 1·24. Temp. = 29·5°. I_{abs} (Intensity of incident radiation in ergs per cm² per sec.) = 1970. d = 0.5 cm.

Concentration of sol		Total I_{abs}.	$K_0 \times 10^{10}$ (obs.).	I_{abs} by unreduced sol only.	* $K_0 \times 10^{10}$ (Calc.).
unreduced.	completely reduced.				
0·05M	0	991	3·49	991	...
0·0475	0·0025M	1017	3·08	862	3·00
0·045	0·005	1036	2·67	743	2·58

* (Calculated taking into account that I_{abs} by the unreduced sol only is effective.)

TABLE III.

With molybdic acid sol.

Glucose = 2·5%. Temp. = 29·5°. p_H = 1·73. $I_{abs.}$ = 1373. d = 0·5 cm.

Concentration of sol		Total $I_{abs.}$	$K_0 \times 10^{10}$ (obs.).	I_{abs} by unreduced sol only.	*$K_0 \times 10^{10}$ (Calc.).
unreduced.	completely reduced.				
0·05M	0	927	2·11	927	...
0·048	0·002M	1261	1·30	539	1·23
0·046	0·004	1346	0·83	343	0·78
0·044	0·006	1373	0·56	251	0·57

We thus see when sol, where the micelles have been completely reduced, is added to the reaction mixture at the beginning of photochemical reaction, the concordance between the calculated and observed values of the velocity constants is only obtained on the assumption that cathodically reduced sol behaves like a pure internal filter.

In our studies of the photochemical reduction of these sols which have been described in the previous papers, the concentration of the reduced sol at the end of the experiment was often greater than 10% of the original sol concentration. Hence if this internal light filter action were operative, the instantaneous velocities of reaction would have diminished continuously until at the end this velocity would have been ½ and ⅓rd. of that at the beginning. But in these reactions, the zero molecular equation was perfectly obeyed during the entire course of the reaction. Hence the explanation holds that so long as unreduced molecules remain in the micelle of a sol, the light quantum absorbed by that micelle is photo-active independently of whether it is absorbed by a molecule of tungstic acid and molybdic acid or their reduced derivatives.

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PHOTOCHEMICAL REACTION WITH SOME INORGANIC COLLOIDS AS ACTIVE AGENTS UNDER THE INFLUENCE OF LIGHT IN VARIOUS STATES OF POLARISATION. PART IX. THE PHOTOCHEMICAL OXIDATION OF ALCOHOL AND GLUCOSE BY IODINE IN ACID MEDIUM WITH TUNGSTIC ACID SOL AS PHOTOSENSITISER.

By J. C. Ghosh, T. Banerjee, S. K. Nandy and N. Guha.

In previous papers, the kinetics of photochemical reduction of some sensitive colloidal solutions have been described. In the present paper are described the results obtained with the same colloidal solutions acting as photosensitisers of oxidation-reduction processes.

The mechanism of reaction is complicated by the fact that the incident radiation is absorbed not only by the photosensitising colloid, but also by the oxidant molecules. These latter, however, have been found to be incapable of effecting oxidation when illuminated alone in the presence of reductant. It is to be concluded, therefore, that only that part of the radiation, which is absorbed by the photosensitive colloidal material, is effective in bringing about the chemical transformation which we have observed.

The fraction of the total light absorbed by the sensitising colloid has been calculated by the approximate formula for the extinction of light by mixtures which is expressed by the equation

$$I_{\text{abs}} \text{ by A} = I_{\text{incident}} \left(1 - e^{-\epsilon_1 C_1 d_1 - \epsilon_2 C_2 d_1} \right) \times \frac{\epsilon_1 C_1}{\epsilon_1 C_2 + \epsilon_2 C_2} \qquad \ldots \quad \text{(A)}$$

The above equation gives the amount of light absorbed by A when mixed with B, the extinction coefficients and concentrations of A and B being, ϵ_1, C_1 and ϵ_2, C_2 respectively.

The influence of the nature of polarisation of the exciting radiations on the photosensitised oxidations was also studied.

This paper embodies our observations on the photo-oxidation of alcohol and glucose by iodine in acid medium using tungstic acid sol as photosensitiser.

EXPERIMENTAL.

The experimental arrangement and procedure were exactly the same as in the previous papers Care was taken to prevent the escape of iodine by volatilisation during the expeiiment by using a well stoppered reaction vessel. The pipetting of reaction mixture was done as quickly as possible. The blank experiments recorded no loss of iodine during this operation. Iodine was estimated by titration as usual with thiosulphate.

There was no reaction when a mixture of iodine solution, hydrochloric acid and a reductant was exposed to ultraviolet rays (366 $\mu\mu$ and 333 $\mu\mu$). Also a mixture of iodine solution, tungstic acid sol and a reductant does not react when kept in the dark for 10 hours The reactions had no induction period except in the case when glucose was used as reductant.

$K_0 = \frac{dx}{dt}$ in the following tables has been expressed as no. of g. mols. transformed per c.c. per sec.

Effect of Varying the Concentration of Iodine.

TABLE I(a).

Alcohol = 4·35M. HCl = 0·063N. Sodium tungstate = 0·021M. Temp. = 33°. I_{abs} (Intensity of radiation absorbed by the reaction mixture in ergs per sq. cm. per sec.) = 1500. d (thickness of the reaction cell) = 1 cm. γ = Quantum efficiency. Mol. ext. coeff. for sodium = 650. Mol ext. coeff. for tungstic acid sol = 556 (*vide infra* Table V).

Conc. of I_2.	I_{abs} by tungstic acid sol.	$K_0 \times 10^{10}$.	γ.	$\frac{1}{K_0/\sqrt{I_{abs}}}$ (by tungstic acid sol).
0·0218N	677	3·64	1·68	$7 \cdot 14 \times 10^{10}$
0·0052	1163	3·54	1·00	$9 \cdot 60 \times 10^{10}$
0·0017	1370	3·00	0·74	$12 \cdot 33 \times 10^{10}$

TABLE I(b).

Glucose = 0·05M. HCl = 0·072N. Temp = 32°. Sodium tungstate = 0·025M. I_{abs} = 2700. d = 1 cm.

Conc. of I_2.	I_{abs} by tungstic acid sol.	$K_0 \times 10^{10}$.	.	$\overline{K_0/\sqrt{I_{abs}}}$ (by tungstic acid sol).
0·046N	857	4·47	1·70	$6 \cdot 55 \times 10^{10}$
0·023	1301	3·89	0·98	$9 \cdot 26 \times 10^{10}$
0·019	1430	3·74	0·86	$10 \cdot 11 \times 10^{10}$
0·012	1730	3·37	0·64	$12 \cdot 35 \times 10^{10}$

FIG. 1.

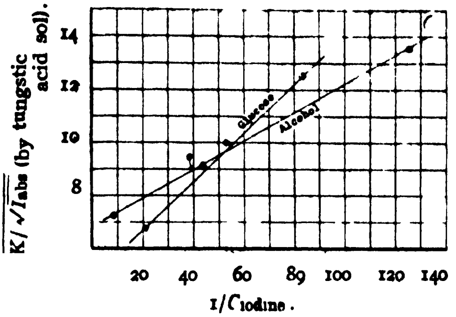
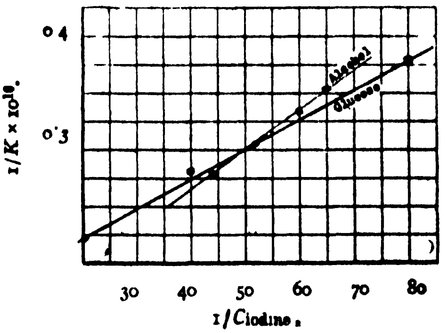


FIG. 2.



It is evident from Fig. 1. that $1/C_{\text{iodine}}$ plotted against $\dfrac{1}{K_0/\sqrt{I_{abs}}}$ (by tungstic acid sol) gives us approximately a straight line.

Effect of Varying the Concentration of Reductant.

TABLE II.

$d=1$ cm.

			Concentration of			
I_{abs}.	Temp.	I_2.	reductant.	HCl.	tungstate.	$K_0 \times 10^{10}$.
			(*a*) Alcohol.			
1500	33°	0·0052*N*	4·35*M*	0·0625*N*	0·021*M*	3·54
,,	,,	,,	3·85	,,	,,	3·27
,,	,,	,,	3·38	,,	,,	3·01
,,	,,	,,	3·1	,,	[illegible]	2·86
			(*b*) Glucose.			
2700	32°	·043*M*	0·05	0·072	0·025	4·47
	,,	,,	0·025	,,	,,	3 52
,,	,,	,,	0·0125	,,	,,	2·68

By plotting $1/K$ against $1/C_R$ we get a straight line (*vide* Fig. 2).

Effect of Varying the Concentration of Acid.

TABLE III.

I_{abs}.	Temp.	I_2.	Concentration of reductant.	HCl.	tungstate.	$K_0 \times 10^{10}$.
(*a*) Alcohol.						
1500	33°	0·0052*N*	4·35*M*	0·125*N*	0·021*M*	2·60
,,	,,	,,	,,	0·0625	,,	3·54
,,	,,	,,	,,	0·042	,,	4·06
(*b*) Glucose.						
2700	32°	0·043	0·05	0·072	0·025	4·47
,,	,,	,,	,,	0·046	,,	5·42
,,	,,	,,	,,	0·024	,,	3·84
,,	,,	,,	,,	0·018	,,	3·47

The p_H of the reacting system at which the velocity was maximum in Table III was found to be 2·1.

Effect of Varying the Intensity of Radiation Absorbed.

TABLE IV.

$d = 1$ cm.

I_{abs}.	Temp.	I_2.	Concentration of reductant	HCl.	tungstate.	$K_0 \times 10^{10}$.
(*a*) Alcohol.						
850	33°	0·0052*N*	4·35*M*	0·0625*N*	0·021*M*	2·54
1500	,,	,,	,,	,,	,,	3·54
(*b*) Glucose.						
1540	32°	0·043	0·05	0·072	0·025	3·21
2700	,,	,,	,,	,,	,,	4·47

Velocity constant varies as the square root of the intensity of radiation absorbed.

Extinction Coefficient.—Extinction coefficient was determined with the help of a Moll thermopile and a Moll galvanometer.

TABLE V.

Substance used.	Mol. extinction coefficient.
Iodine	650
Tungstic acid sol	556

Quantum Efficiency of the Reaction.

Quantum efficiency (γ) of the reactions is given in Table I.

One typical example is given below.

In Table I (*a*), the intensity of absorbed radiation per sq. cm. per sec. $=1500$

$$=\frac{1500\times 366\times 10^{-7}}{(6{\cdot}55\times 10^{-27})\times(3\times 10^{10})\times(6{\cdot}1\times 10^{23})}$$

$$=4{\cdot}58\times 10^{-10} \text{ Einstein.}$$

Of this absorbed radiation, the part absorbed by tungstic acid sol which alone is responsible for these photo oxidations

$$=4{\cdot}58\times 10^{-10}\times\frac{556\times 0{\cdot}021}{556\times 0{\cdot}021+0{\cdot}021\times 650} \text{ from eqn. } \ldots \quad (1)$$

$$=2{\cdot}15\times 10^{-10} \text{ Einstein.}$$

($\epsilon_{\text{tungstic acid sol}}=556$; $\epsilon_{\text{iodine}}=650$, *vide* Table V).

The zero-molecular velocity constant K_0 (expressed in terms of no. of g. mols. transformed in 1 sec. in 1 c. c.) $=3{\cdot}74\times 10^{-10}$; $d=1$ cm.

$$\gamma=\frac{3{\cdot}74\times 10^{10}}{2{\cdot}15\times 10^{10}}=1{\cdot}74$$

Effect of Varying the Temperature.

TABLE VI.

(*a*) ***With alcohol*** : Alcohol $=4{\cdot}35M$. Tungstate $=0{\cdot}021M$. Iodine $=0{\cdot}0052N$. $HCl={\cdot}0625N$. $I_{abs.}=1500$

(*b*) ***With Glucose*** : Glucose $0{\cdot}05M$ Tungstate $=0{\cdot}025M$. Iodine $=0{\cdot}043N$. $HCl=0{\cdot}072N$. $I_{abs}=2700$.

Temp.	*K*.	Temp. coeff. K_{T+10}/K_T	Temp.	*K*.	Temp. coeff. K_{T+10}/K_T
28°	2·76	...	32°	4·47	..
33°	3·65	1·64	39°	5·79	1·80
38°	4·54	...	42°	8·04	...
(Calc.)			(Calc.)		

Temperature coefficient is rather high being of the order of 1·6 and 1·8, when the reductants used are alcohol and glucose respectively.

Comparison of the Effect of Various States of Polarisation of Light on the Velocity of Reaction.

TABLE VII.

Iodine = 0·0052N. Tungstate = 0·021M. Alcohol = 4·35N. HCl = 0·0625N d = 1 cm. Temp. = 33°.

State of polarisation.	I_{abs}.	$K_0 \times 10^{10}$.
l-Circularly polarised light	310 ergs/cm.^{2}/sec.	1·36
d-Circularly polarised light	310	1·05

TABLE VIII.

Tungstate = 0·025M. Iodine = 0·043N. HCl = 0·072N. Glucose = 0·05M. Temp. = 32°. d = 0·5 cm.

Nature of light used.	I_{abs}.	$K_0 \times 10^{10}$.
Unpolarised	2700	4·47
l-Circularly polarised	570	2·05
d-Circularly polarised	570	1·74
l-Circularly polarised	360	1·63
d-Circularly polarised	360	1·37

From Tables VII and VIII, it is evident that $V_l > V_d$, the terms having Their usual significance.

The reaction has the following characteristics.

(1) The velocity is proportional to the square root of the intensity of radiation absorbed.

(2) The inverse of velocity plotted against the inverse of concentration of reductant is a straight line.

(3) Temperature coefficient of the reactions is of the order of 1·8.

(4) The velocity of reaction for the same intensity of absorbed radiation is larger for *l*-circularly polarised light than for *d*-circularly polarised light.

Thesecharacteristics of the reaction can be explained on the assumption that the radiation absorbed by the particles of tungstic acid sol is communicated to the mols of iodine adsorbed on their surface which thereby get dissociated into iodine atoms.

The mechanism of subsequent reactions is similar to that postulated by Ghosh and Purkayastha for photobromination of lactic acid (*J. Indian Chem. Soc.*, 1929, **6**, 375, 383).

I_2 (adsorbed on the surface of tungstic acid micelles) + $h\nu$ (absorbed by tungstic acid sol micelles) $\longrightarrow$ 2I ... (*i*)

$2\,I \longrightarrow I_2$ ... ... (*ii*)

$I + I_2$ (adsorbed on the surface of tungstic acid micelles) $\longrightarrow I_3$ ... (*iii*)

$I_3 \longrightarrow I_2 + I$ ... ... (*iv*)

I_3 + Reductant (adsorbed on the surface of micelles) $\longrightarrow$
oxidised product + 2 HI + I ... ... (*v*)

$\frac{dx}{dt}$ for reaction (*v*) is given by the equation

$$\left[\sqrt{K_2\,\frac{I_{\text{abs (by tungstic acid sol}}}{Nh\nu}}\right]\left[\frac{K_3 C_s^{I_2}}{K_5 C_s^{R} + K_3}\right]\left[K_5 C_s^{R}\right]$$

where $C_s^{I_2}$ = surface conc. of the iodine molecules

C_s^{R} = ,, ,, ,, reductant ,,

Assuming that the surface concentration of I_2 is also given by Langmuir's equation

$$= \frac{K' C_s^{I_2}}{K'' + K''' C_s^{I_2}}$$

where $C_s^{I_2}$ = the bulk conc. of iodine molecules. The final equation for the velocity becomes

$$K_0 = \frac{dx}{dt} = \left[\sqrt{K_2 \frac{I_{\text{abs (by tungstic acid sol)}}}{Nh\nu}} \right] \left[\frac{K_5 C_s^{R}}{K_5 C_s^{R} + K_3} \right]$$

$$\times \left[\frac{K_6 C_s^{I_2}}{K_8 C_s^{I_2} + K_7} \right]$$

Hence in presence of excess of reductant,

$$\frac{1/K_0}{\sqrt{K_2} \times \frac{I_{\text{abs (by tungstic acid sol)}}}{Nh\nu}}$$ plotted against $1/C_{\text{iodine}}$

should give us a straight line

i.e., $$\frac{1/K_0}{\sqrt{I_{\text{abs (by tungstic acid sol)}}}}$$ plotted against $1/C_{\text{iodine}}$

should give us a straight line, the other terms being constant. This has been experimentally realised (*vide* Tables IA, IB and Fig. 1).

The velocity also varies as the square root of light absorbed by the tungstic acid sol and the reciprocal of the velocity plotted against the reciprocal of the concentration of the reductant under otherwise identical conditions gives a straight line.

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PHOTOCHEMICAL REACTION WITH SOME INORGANIC COLLOIDS AS ACTIVE AGENTS UNDER THE INFLUENCE OF LIGHT IN VARIOUS STATES OF POLARISATION. PART X. ON THE PHOTOCHEMICAL OXIDATION OF GLUCOSE BY POTASSIUM INDIGO-TETRASULPHONATE WITH TUNGSTIC ACID SOL AS PHOTOCATALYST.

By J. C. Ghosh, T. Banerjee and S. K. Bhattacharjee.

Experimental arrangement was the same as in Part I of this series. Pure potassium indigo-tetrasulphonate (supplied by British Drug House) was used in this investigation.

Spectrophotometric method was adopted for the estimation of potassium indigo-sulphonate at any moment. The green region of the spectrum (525 $\mu\mu$) was chosen for this purpose, the *leuco*-dye having no extinction at this region. By plotting the ordinary spectrophotometric term log tan θ_2 − log tan θ_1 (θ_1 being obtained with water only) against concentration of the dye, a straight line was obtained. From this curve (Fig. 1), the concentration of potassium indigo-tetrasulphonate at any moment was calculated from the spectrophotometer reading at that moment.

Fig. 1.

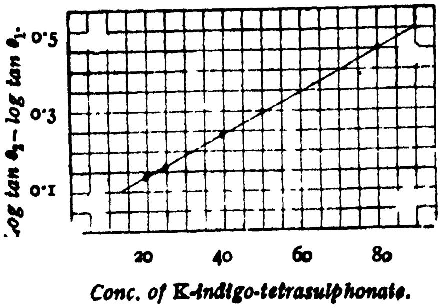


TABLE I.

K-indigo-tetra-sulphonate.	Spectrophoto-meter readings. (with soln. in the cell θ_2).	Spectrophoto-meter readings. (with water in the cell θ_1).	$\text{Log}\frac{\tan\theta_2}{\tan\theta_1}$.
$80{\cdot}0 \times 10^{-6}M$	70°·0	45°·5	0·4314
$66{\cdot}0 \times 10^{-6}$	67°·2	,,	0·3689
$50{\cdot}0 \times 10^{-6}$	63°·0	,,	0·2853
$40{\cdot}0 \times 10^{-6}$	59°·5	,,	0·2224
$25{\cdot}0 \times 10^{-6}$	55°·0	,,	0·1473
$20{\cdot}0 \times 10^{-6}$	54·5	,,	0·1392

The cell containing the reaction mixture was made absolutely air-tight as *leuco*-indigo is easily oxidised by air. It was observed that potassium indigo-tetrasulphonate does not get reduced when exposed to the light of wave-length 366 $\mu\mu$ in presence of either tungstic acid sol or glucose separately. No dark reaction was observed when a mixture of glucose, potassium indigo-tetrasulphonate, sodium tungstate and hydrochloric acid was kept in the dark for more than 12 hours.

The extinction coefficient for 366 $\mu\mu$ of *leuco*-indigo-sulphonate is very much greater than that of potassium indigo-sulphonate as determined by Moll thermopile and galvanometer. This will be evident from Table II.

TABLE II.

Substance taken.	Mol. ext. coeff. at 366 $\mu\mu$.
Pot.-indigo-tetrasulphonate	6,485 (e_2)
leuco-Indigo-tetrasulphonate	27,594 (e_3)
Tungstic acid sol	556 (e_1)

The equation used in this paper is derived thus :—

$$\frac{dx}{dt} = K' I \text{ (fraction of light absorbed by tungstic acid sol)} \times C_s^n$$

$$K I \frac{e_1 [T]}{e_1 [T] + e_2 (a - x) - e_3 x} \times C_s^n$$

$$= K.I. \frac{\epsilon_1 [T]}{\{\epsilon_1 [T] + \epsilon_2 a\} - (\epsilon_3 - \epsilon_2) x} \times C_s^R$$

$$= K I \;.\; \frac{A}{A' + Bx} \;.\; C_s^R$$

where $A = \epsilon_1 T$

$B = \epsilon_3 - \epsilon_2$

$A' = A + \epsilon_2 a$ (a, being the initial concentration of pot.indigo-tetrasulphonate).

and C_s^R is the surface conc. of reductant on the photoactive micelle.

The above equation on integration gives

$$K I C_s^R = \frac{A' x + \frac{Bx^2}{2}}{A t}$$ where t is reckoned in secs.

For the same concentration of reductant present in excess,

$$K'I = \frac{A'x + \frac{Bx^2}{2}}{A t} \qquad \ldots (i)$$

TABLE III.

Experimental Results.

Tungstate = 0·03M. Glucose = 0·125M. HCl = 0·0478N. Indigo-tetrasulphonate = $37·6 \times 10^{-5}M$. p_H of the system = 3·6. Temp. = 33°. I_{abs} (Intensity of absorbed radiation in ergs/cm^2/sec.) = 8230.

	Time.	Pot. indigo-sulphonate.	$K \times 10^7$ [from (i)].	$K \times 10^7$ (mean).
1.	0 sec.	37·6 $M \times 10^{-5}$		
2.	600	30·8	1·43 (from 1 & 2)	
3.	1560	20·9	1·35 (from 1 & 3)	1·40
4.	2400	11·4	1·40 (from 1 & 4)	

The above table shows that the equation (i) can be successfully applied to this particular reaction.

TABLE IV.

Effect of varying the concentration of Pot. indigo-tetrasulphonate.

Temp. = 33°, p_H = 3·61. Region − 366$\mu\mu$. Tungstate = 0·03M. HCl = 0·0478M.

Conc. of glucose.	Conc. of indigo × 10^5.	I_{abs}.	$K \times 10^7$ (i)
(a) 0·125M	76·9M	8230 ergs	1·45
,,	59·0	,,	1·43
,,	37·6	,,	1·40
(b) 0·5M	82·3	7130	2·50
,,	37·4	,,	2·43

From Table IV it is evident that velocity constant is independent of the concentration of indigo-tetrasulphonate.

TABLE V.

Effect of varying the concentration of glucose.

Temp. = 33°. p_H = 3·6. Region – 366$\mu\mu$. d = 0·5 cm. Tungstate = 0·03M, HCl = 0·0478N.

	Conc. of Glucose.	Conc. of indigo × 10^5.	I_{abs}.	$K \times 10^7$ (t)
(a)	0·5M	37·4 × 10^5 M	6650 ergs	2·19
	0·25	,,	,,	1·58
	0·125	,,	,,	1·10
	0.0625	,,	,,	0·70
(b)	0·5M	72·0 × 10^5 M	3973	1·46
	0·25	,,	,,	0·98
	0·125	,,	,,	0·702

1/K plotted against 1/C gives a straight line. (Fig. 2).

TABLE VI.

Effect of varying the concentration of HCl.

Temp. = 33°. I_{abs} = 7130. Tungstate = 0·03M. Glucose = 0·125M. Dye = 82·3 × $10^{-5}M$.

Conc. of HCl.	p_H.	$K \times 10^7$ (t)
0·0478M	3·61	1·18
0·061	2·0	5·52
0·093	1·57	3·97

The velocity passes through a maximum at p_H = 2.

Temperature Coefficient of the Reaction.—The temperature coefficient is of the order of unity.

TABLE VII.

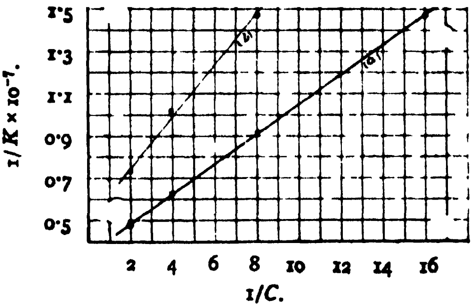
Effect of Varying the Intensity of Radiation absorbed.

Temp. = 33°. p_H = 3·61. Region – 366$\mu\mu$. Tungstate = 0·03M. HCl = 0·0478M.

	(a)		(b)		(c)	
I_{abs}.	3973	2520	8230	3973	8230	6650
Conc. of glucose (M)	0·5	0·5	0·125	0·125	0·125	0·125
Conc. of indigo × 10^5 (M)	76·9	76·9	76·9	76·9	37·0	37·0
$K \times 10^7$ (t).	1·46	0·93	1·43	0·702	1·40	1·10

The velocity constant, as is evident from the above table, is proportional to the intensity of radiation absorbed.

FIG. 2.



Quantum Efficiency of the Process.

Quantum efficiency is much less than unity.

A typical case (Table IV*b*) taken from the composition of the reaction mixture is given below :—

Conc. of tungstate $=0\cdot03M$. Conc. of HCl $=0\cdot0478M$.

Conc. of glucose $=0\cdot5\ M$. Conc. of dye $=82\cdot3\times10^{-5}M$.

$p_H=3\cdot61$. Mean wave-length $=366\mu\mu$. Energy absorbed $=7134$ ergs. per cm^2/sec.

The reaction cell is 0'5 cm. thick and 2'7 sq. cm. in area.

Fraction of light quanta absorbed by tungstic acid sol per sec. per unit area

$$=\frac{7134\times366\times10^{-7}\times2\cdot7}{6\cdot5\times10^{-27}\times3\times10^{10}}\left[\frac{\epsilon_1\,[T]}{\epsilon_1[T]+\epsilon_2[\text{Indigo}]+\epsilon_3\,[\text{leucodye}]}\right]$$

$$=36\cdot09\times10^{14}\times0\cdot58=20\cdot9\times10^{14}.$$

The initial conc. of indigo $=82\cdot3\times10^{-5}M$.

After 31 mins. the conc. became $=50\cdot5\times10^{-5}M$.

At that time $a-x = 50{\cdot}5 \times 10^{-5}\ M$ (conc. of indigo-sulphonate)

$x = 31{\cdot}8 \times 10^{-5}\ M$ (conc. of leuco-dye)

The no. of mols. transformed per sec.

$$= \frac{0{\cdot}5 \times 2{\cdot}7 \times 31{\cdot}8 \times 10^{-5} \times 6{\cdot}1 \times 10^{23}}{1000 \times 31 \times 60}$$

$$= 1{\cdot}40 \times 10^{14}$$

$$\therefore\ \gamma(\text{Quantum efficiency}) = \frac{\text{No. of mols. transformed}}{\text{No. of quantum absorbed}}$$

$$= \frac{1{\cdot}4 \times 10^{14}}{20{\cdot}9 \times 10^{14}} = 0{\cdot}067.$$

Dependence of the Velocity of Reaction on the State of Polarisation of Light.

TABLE VIII.

Region = 366$\mu\mu$. Tungstate = 0·03M. HCl = 0·0478N. Glucose = 0·5M. K-indigo sulphonate = $76{\cdot}8 \times 10^{-5} N$. $p_H = 3{\cdot}61$.

Nature of light.	$I_{abs.}$	$K \times 10^7$ (f)
Unpolarised	3973	1·46
l-Circularly polarised	1030	0·302
d-Circularly polarised	1030	0·197

TABLE IX.

Region = 366$\mu\mu$. Tungstate = 0·02M. HCl = 0·0318N. Temp. = 33°. Glucose = 0·25M. K-indigo-sulphate = $34{\cdot}6 \times 10^{-5}\ N$. $p_H = 3{\cdot}83$.

Nature of light.	$I_{abs.}$	$K \times 10^7$ (f)
Unpolarised	3970	2·88
l-Circularly polarised	990	0·543
d-Circulrrly polarised	990	0·415

From Tables VIII and IX we find that $V_L > V_D$, the terms having their usual significance.

DISCUSSION.

Any mechanism of reaction that may be proposed for this photochemical oxidation should be in a position to explain the following facts:

(*a*) The velocity constant is given by the equation

$$K'I = \frac{A'x + Bx^2/2}{A \cdot t} \qquad \text{Eqn.} \ \ldots \ (i)$$

(*b*) The velocity constant increases as the concentration of glucose increases. If $1/K$ is plotted against $1/C_{\text{glucose}}$, a straight line is obtained.

(*c*) The velocity passes through a maximum at p_H 2.

(*d*) The temperature coefficient of the reaction is unity.

(*e*) The velocity constant is proportional to the intensity of radiation absorbed.

(*f*) Quantum efficiency is very low.

The sol surface is completely covered with a unimolecular layer of the dye molecules even at very low concentration of the dye. It is remarkable that the absorption of radiation by the dye molecules directly does not lead to their photoreduction by reaction with glucose. But a dye molecule can be brought into an activated state by receiving energy from the elementary spaces of tungstic acid sol surface which is also excited by the absorption of a quantum of radiation.

The initial velocity of reaction is given by

$$\frac{dx}{dt} = K_1 C_s^a I$$

where I is the radiant energy absorbed per sec. by the elementary spaces of the tungstic acid sol surface and C_s^a, the surface concentration of reductant.

But with the progress of reaction, the *leuco*-dye is formed and the photosensitive sol surface begins to be covered with the molecules of *leuco*-dye, The fraction of the surface so covered by the *leuco*-dye becomes useless for purpose of photoreduction and hence

$$\frac{dx}{dt} = K_1 C_s^s \, I_0 \frac{\epsilon_1 [T]}{\epsilon_1 [T] + \epsilon_2 (a-x) + \epsilon_3 x}$$

which on integration gives the equation (*i*).

This equation (*i*) has been found to hold good.

The rate of oxidation of glucose also depends on the surface concentration of glucose.

But since, according to Langmuir's hypothesis, C_s^s is given by

$\frac{K_3 C_s^0}{K_4 + K_5 C_s^0}$ where C_s^0 is the bulk concentration of glucose in solution.

$1/K'$ plotted against $1/C_{\text{glucose (bulk)}}$ should give a straight line which has been found to be true.

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PHOTOCHEMICAL REACTION WITH SOME INORGANIC COLLOIDS AS ACTIVE AGENTS UNDER THE INFLUENCE LIGHT IN VARIOUS STATES OF POLARISATION. PART XI. THE PHOTOCHEMICAL OXIDATION OF GLUCOSE BY METHYLENE BLUE WITH URANIC ACID SOL AS PHOTOSENSITISER.

By J. C. Ghosh, T. Banerjee and J. C. Bose.

Uranic acid sol was prepared as described before (*vide* Part IX, p. 581).

The change in the concentration of methylene blue was followed spectrophotometrically. The graph (Fig. 1) was obtained by plotting different concentrations of methylene blue in presence of a certain concentration of uranic acid (0·021*M*) against log tan α − log tan α' [α=angular displacement with dye of a particular strength in presence of uranic acid (0·021*M*) and α'=that with uranic acid (0·021*M*) at $\lambda=525\mu\mu$]. Uranic acid (0·042-·0021*M*) has little absorption at $525\mu\mu$. And moreover as the concentration of uranic acid was constant during the course of reaction, the presence of uranic acid did not affect the estimation of methylene blue by this method. When uranic acid was changed, a separate standard graph was obtained for each case.

No reduction was observed when a solution of methylene blue (Merck's chemically pure sample) alone was exposed to ultraviolet light (366 $\mu\mu$). There was no reaction when a mixture of uranic acid and methylene blue and glucose (Kahlbaum's pure anhydrous sample) was exposed to ultraviolet light. A mixture of glucose, uranic acid and methylene blue does not react when kept in the dark for about 14 hours.

A large induction period was observed in the photochemical reaction.

RESULTS.

Effect of Varying the Concentration of Methylene Blue.

TABLE I.

Temp. $=32°$. Methylene blue $=0{\cdot}000612\ M$. Glucose $=0{\cdot}025\ M$. Uranic acid sol $=0{\cdot}021 M$. $^{*}I_{abs.}=1180$. d (thickness of the reaction cell) $=0{\cdot}5$ cm.

	Time.	Readings of spectrophotometer.	Concentration of M.B.	K (zero-molecular with respect to M.B.). $\times 10^{10}$
1.	0 mins.	65·0	0·000612M	1
2.	45	63·0	0·000549	1·92 (from 2 and 3).
3.	60	58 1	0·000377	1·97 (from 3 and 4).
4.	75	52·5	0·000200	
				Mean 1·95

* I_{abs} = Intensity of absorbed radiation in ergs/cm²/sec. [M.B. denotes methylene blue].

Similar readings were taken with other concentrations of methylene blue and the results are given below. The zero-molecular velocity constant was expressed in terms of no. of g. mols of methylene blue transformed in 1 sec. in a unit cell.

TABLE II.

Glucose $=0{\cdot}025 M$. Uranic acid sol $=0{\cdot}021 M$.

Methylene blue $\times 10^{-4} (M)$	...	7·46	7·35	6·12	5·75	4·90	4·28
K (zero-mol.) $\times 10^{10}$	...	1·98	2·02	1·95	1·88	2·00	1·92
Quantum efficiency (γ)	...	0·97	1·00	0·97	0·94	0·97	0·94

The zero-molecular velocity constant does not undergo any change with change in the concentration of methylene blue.

TABLE III.

Effect of varying the concentration of glucose.

Temp. $=32°$. $I_{abs}=1180$.
Me blue $=6{\cdot}12\times10^{-4} M$.
Uranic acid sol $=0{\cdot}021\ M$.

Glucose (M)	0·025	0·0125	0·0063
K (zero-mol.) $\times 10^{10}$	1 95	1·25	0·70
γ	0·97	0·62	0·34

TABLE IV.

Effect of varying the concentration of uranic acid sol.

Temp. $=32°$. $I_{abs}=1180$.
Glucose $=0{\cdot}025M$
Me blue $=6{\cdot}12\times10^{-4} M$.

Uranic acid sol (M)	0·042	0·021
K (zero-mol.) $\times 10^{10}$	2·17	1·95
γ	1·08	0·97

It is found that 1/*K* plotted against 1/conc. of glucose gives a straight line (Fig. 2).

Fig .1.

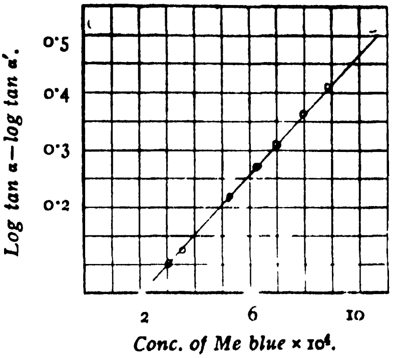
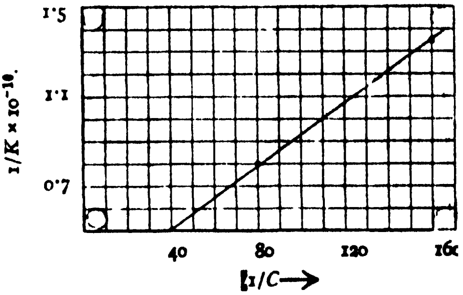


Fig. 2.



The zero-molecular constant diminishes slightly as the concentration of uranic acid sol is diminished.

Effect of Varying the Temperature.—The temperature coefficient is very small being of the order of 1·05−1·15.

Effect of Varying the Intensity of Radiation.

Table V.

Me blue = $6·12 \times 10^{-4}M$. Glucose = $0·025M$. sol. = $0·021M$. Temp. = 32°.

I_{abs}.	K (zero-molecular) × 10¹⁰.
1180 ...	... 1·95
370 ...	... 0·57

It will be seen from the above table that the velocity constants vary directly as the intensity of absorbed radiation.

The molecular extinction coefficient of uranic acid and methylene blue at 366μμ were measured with the help of a Moll thermopile and a Moll Galvanometer. The results are given in Table VI.

TABLE VI.

Absorbing substance.	Mol. ext. coeff. (366μμ).
Uranic acid sol	28
Methylene blue	2500

Quantum Efficiency of the Process.

In Table I, the intensity of total radiation (366μμ) absorbed by a solution of 0·5 cm. thick = 1180 ergs. per sq. cm. per sec. = $3{\cdot}603 \times 10^{-10}$ Einstein per sq. cm. per sec.

Now the part of the energy absorbed by uranic acid only is effective in bringing about the photochemical change and is approximately

$$= 3{\cdot}603 \times 10^{-10} \times \frac{0{\cdot}021 \times 28}{0{\cdot}021 \times 28 + 6{\cdot}12 \times 10^{-4} \times 0{\cdot}25 \times 10^{4}}$$

$= 1{\cdot}015 \times 10^{-10}$ Einstein per sq. cm. per sec.,

the mol. extinction coefficients of uranic acid and methylene blue being 28 and 2500 respectively.

Since the zero-molecular velocity constant K (expressed in terms of no. of g. mols transformed in 1 sec. in a unit cell (1 cm. × 1 cm. × 1 cm.) $= 1{\cdot}95 \times 10^{-10}$.

No. of g. mols transformed in 1 sec. in a cell (1 cm × 1 cm × 0·5 cm.) $= 0{\cdot}98 \times 10^{-10}$, the thickness of the reaction cell being 0·5 cm. Quantum efficiency of the process

$$= \frac{0{\cdot}98 \times 10^{-10}}{1{\cdot}015 \times 10^{-10}} = 0{\cdot}97.$$

Quantum yield for other experiments were similarly calculated.

TABLE VII.

Dependence of the velocity of radiation on the state of polarisation.

Nature of light.	I_{abs}.	K (zer-omol.) with respect to Me blue.
Unpolarised	1180	$1{\cdot}95 \times 10^{10}$
l-Circularly polarised	220	0·367
d-Circularly polarised	220	0·350

It will be seen from the above table that the velocity constant is not much affected by the nature of the activating light.

DISCUSSION.

The photochemical reaction between methylene blue and glucose with uranic acid sol as photosensitiser is characterised by great simplicity.

(1) The reaction is zero-molecular with respect to methylene blue. (2) The velocity is proportional to the intensity of light absorbed, (3) and is practically independent of the concentration of uranic acid sol provided that the sol strength is such as to ensure complete absorption of incident radiation. The quantum efficiency is of the order of unity. The mechanism of reaction must necessarily be the following :—

Methylene blue even in very small concentrations forms as in the case with most dyestuffs, a saturated unimolecular layer on the sol surface. The excited elementary spaces of the uranic acid sol surface, produced by the absorption of a quantum o radiation, activates a molecule of methylene blue adsorbed on the surface. These activated molecules of methylene blue on the surface of the sol particle react with a molecule of reductant also adsorbed on the surface of the sol.

The velocity of reaction is given by

$$\frac{dx}{dt} = K . \frac{I}{Nh\nu} . C_s^a = K \qquad \dots \quad (i)$$

where C_s^a is the surface concentration of glucose.

According to Langmuir, $C_s^a = \dfrac{K_1 C_s^e}{1 + K_2 C_s^e}$ ... (ii)

where C_s^e is the concentration of glucose in solution.

Hence $\frac{1}{K} = \frac{1}{K_1 C_s} + \frac{K_2}{K_1}$ ... ... (*iii*)

i.e., the inverse of velocity constant plotted against the inverse of glucose concentration should give a straight line, which has been found to be the case.

The velocity of reaction has been found to be proportional to the intensity of radiation as is demanded by the equation (*i*). The quantum efficiency of the reaction involving the action of uranic acid sol as a photo-catalyst is independent of the state of polarisation of exciting radiation.

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PHOTOCHEMICAL REACTION WITH SOME INORGANIC COLLOIDS AS ACTIVE AGENTS UNDER THE INFLUENCE OF LIGHT IN VARIOUS STATES OF POLARISATION. PART XII. THE PHOTOCHEMICAL OXIDATION OF GLUCOSE AND LAEVULOSE BY METHYLENE BLUE WITH FERRIC HYDROXIDE SOL AS THE PHOTO-SENSITISER.

By T. Banerjee, S. K. Bhattacharjee and N. Mukherjee.

Preparation of Ferric Hydroxide Sol.

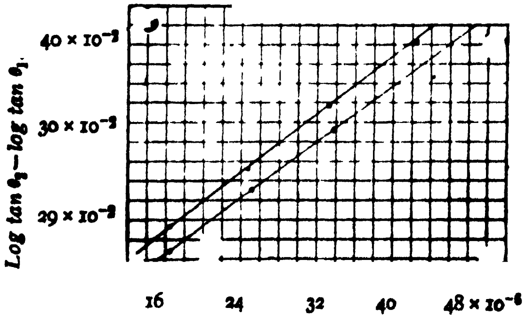
The sol was prepared after Dumansky (*J Russ Phys. Chem. Soc.*, 1904, **34**, 1067). A dilute solution of Merck's 'extra pure' ferric chloride was treated with Merck's extra pure ammonium carbonate in the cold until the precipitate formed just dissolved. The deep red coloured sol thus formed was filtered and then subjected to hot dialysis at 70°-80° for 12 days.

Estimation of Ferric Hydroxide Sol.

The ferric hydroxide sol was gravimetrically estimated as Fe_2O_3 (Treadwell, 1924 Ed., p. 94). The sol was also iodometrically estimated by Carl Mohr's method (*Ann. Chem. Pharm.*, **105**, 53). The results obtained by the two methods were found to be identical.

Spectrophotometric readings were taken with the quartz cell filled with water or mixtures of different concentrations of methylene blue and ferric hydroxide sol in the red region of the spectrophotometer (632 $\mu\mu$) where the absorption due to the sol was the smallest. A graph (Fig. 1) was obtained

Fig. 1.



by plotting $\log \tan \theta_2 - \log \tan \theta_1$ against the concentrations of methylene blue at a particular sol concentration. A separate graph was traced with each concentration of the sol (*cf.* Part XIII).

A solution of methylene blue or methylene blue and glucose or methylene blue and ferric hydroxide remained unaffected when exposed to the radiation of wave-length $366\mu\mu$ and $254\mu\mu$. A mixture of glucose, ferric hydroxide sol and methylene blue does not react when kept in the dark for 24 hours.

RESULTS.

A very long induction poriod (from 6 hours to 14 hours depending upon the intensity of exciting light) was observed in the photochemical reaction even when the air in the reaction mixture was removed by passing nitrogen through it. In the following experiments, the induction period was considerably minimised (from 6 hours to less than 2 hours) by pre-exposing the reaction mixture to sunlight for 5 minutes.

TABLE I.

Reaction mixture not pre-exposed to sun-light. *d* (thickness of the reaction cell) = 0·5 cm. Composition of reaction mixture:—Sol (as Fe_2O_3) $= 0{\cdot}0107M$; glucose = 1%; methylene blue $= 50 \times 10^{-6}M$. $p_H = 4{\cdot}8$. Temp. = 29°. $^*I_{abs} = 2352$.

Time.	Spectrophotometric reading. (θ_2)	Zero reading. (θ_1)	Conc. of methylene blue × 10^6.	K_0 (no. of mols transformed per c.c. per sec.) × 10^{12}.
(1) 0 hr.	74·5	51·5		
(2) 6	66·5	,,		
(3) 6½	63·5		22·0	
(4) 7	60·5	,,	15·6	3·56 (from 3 & 4)
(5) 7½	57·0	,,	9·5	3·38 (from 4 & 5)
				Mean – 3·37

The reaction is zero-molecular with respect to methylene blue.

---

* I_{abs}, here and in the following tables denotes the intensity of radiation absorbed by the reaction mixture in ergs per sq. cm. per sec.

Effect of Varying the Concentration of Reductant.

TABLE II.

Temp.$=29°$. Sol$=0·0107M$. Methylene blue $=50\times10^{-6}M$.
$p_H = 4·8$. I_{abs} at 254 $\mu\mu = 1380$ and at $366\mu\mu = 2160$. $d = 0·5$ cm.
γ=quantum efficiency.

Conc. of reductant.	$K\times10^{13}$ at $254\mu\mu$.	γ at $254\mu\mu$.	$K\times10^{13}$ at $366\ \mu\mu$.	γ at $366\mu\mu$.
Glucose.				
8%	—	—	3·80	0·00282
4	1·48	0·00252	3·80	0·00282
2	1·49	0·00263	3·78	0·00282
1	1·33	0·00226	3·02	0·00225
0·5	1·075	0·00183	2·53	0·00189
0·25	0·767	0·00130	1·65	0·00125
Laevulose				
1%	...	...	10·00	0·0075
0·5	4·48	0·0094	9·93	0·0075
0·25	4·48	0·0094	9·93	0·0075
0·125	3·92	0·0066	9·38	0·0070
0·0625	3·05	0·0052	8·30	0·0062
0·0313	2·45	0·0042	6·82	0·0051

From the above table it will be found that upto a certain concentration of the reductant, the velocity constant does not undergo any change with change in concentration of the reductant. Below this limiting concentration of the reductant, the velocity constant diminishes with the decrease in the concentration of reductant and $1/K$ plotted against $1/C$ gives a straight line (Figs. 2 and 3).

FIG. 2.

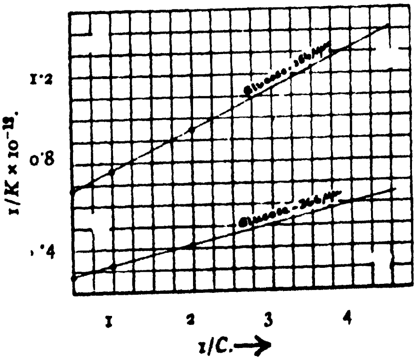
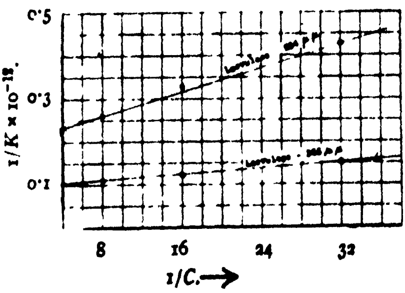


FIG. 3.



Effect of Varying the Concentration of Sol.

TABLE III.

Temp. = 29°. Methylene blue = $50 \times 10^{-6} M$.

Wave-length.	Conc. of sol.	Reductant.	p_H.	I_{abs}.	$K \times 10^{12}$.
		Glucose.			
254 $\mu\mu$	0·0107 *M*	1%	4·80	1366	1·365
,,	0·0054	,,	4·86	1352	1·275
366 $\mu\mu$	0·0107	,,	4·80	2496	3·497
,,	0·0054	,,	4·86	2482	3·242
		Laevulose.			
254 $\mu\mu$	0.0107	0·25%	4·80	1366	4·47
,,	0·0054	,,	4·86	1352	4·15
366 $\mu\mu$	0·0107	,,	4·80	2163	10·08
,,	0·0054	,,	4·86	2158	9·67
,,	0·0017	,,	4·95	2145	9·35

From the above table it is evident that the velocity constant diminishes slightly with diminishihg concentration of the sol, the intensity of radiation absorbed by the sol also diminishing slightly.

Effect of Varying the p_H of the Reacting System.

TABLE IV.

Temp. = 29°. Sol = 0·0107 *M*. Methylene blue = $50·0 \times 10^{-6}$ *M*.

I_{abs} at 254 $\mu\mu$ = 1380 and at 366 $\mu\mu$ = 2544 with glucose, and at 366 $\mu\mu$ = 2032 with laevulose.

p_H.	Reductant. Glucose.	$K \times 10^{12}$ at 254 $\mu\mu$.	γ at 254 $\mu\mu$.	$K \times 10^{12}$ at 366 $\mu\mu$.	γ at 366 $\mu\mu$.
5·5	1%	1·00	0·00166	2·00	0·00014
5·1	,,	1·17	0·00198	2·69	0·00166
4·8	,,	1·33	0·00228	3·55	0·00223
4·5	,,	0·99	0·00166	...	...
4·3	,,	...	...	1·68	0·00100
4·0	,,	0·0	0·0	0·0	0·0
	Laevulose.				
5·5	0·25%	3·1	0·0052	6·30	0·0050
5·1	,,	...	...	7·47	0·0069
4·8	,,	4·48	0·0092	9·33	0·0074
4·3	,,	2·70	0·0045	4·20	0·0033
4·0	,,	0·0	0·0	0·0	0·0

From the above table it is evident that the velocity constant passes through a maximum to almost zero as the p_H of the system decreases. The maximum velocity constant is obtained at p_H 4·8.

Effect of Varying the Intensity of Absorbed Radiation.

The intensity of radiation (366 $\mu\mu$) absorbed by the reaction mixture was measured by noting the deflections of a Moll galvanometer connected with a Moll thermopile placed behind the reaction cell, first with the cell filled with pure water and then with the reaction mixture. The difference gave the light absorbed by the reaction mixture (*vide* Part I).

The energy of total incident radiation of 254 $\mu\mu$ was similarly measured with a Moll thermopile and a Moll galvanometer. The galvanometer deflections were noted with the cell, first filled with pure water and then with normal potassium nitrite solution which absorbed completely the extreme ultraviolet radiation (254 $\mu\mu$). The difference gave the intensity of total ultraviolet radiation (254 $\mu\mu$).

The amount of light absorbed by ferric hydroxide sol alone was calculated by the approximate extinction formula for mixtures. I_{abs} by ferric hydroxide sol (A).

$$=I_{\text{incident}}\left(1-e^{-\overset{\lambda}{\epsilon_1}c_1d_1-\overset{\lambda}{\epsilon_2}c_2d_2}\right)\times\frac{\overset{\lambda}{\epsilon_1}c_1}{\overset{\lambda}{\epsilon}c_1+\overset{\lambda}{\epsilon}c_2}\qquad\ldots\quad(A)$$

the extinction coefficients (at wave length λ) and concentrations of A and B (the other absorbing agent) being $\overset{\lambda}{\epsilon_1}$, c_1 and $\overset{\lambda}{\epsilon_1}$ and c_2 respectively.

Molecular extinction coefficient of ferric hydroxide sol and methylene blue in the ultraviolet were measured by means of a Hilger quartz spectrograph in conjunction with a rotating sector. The values are given in Table V and Fig. 4.

FIG. 4.

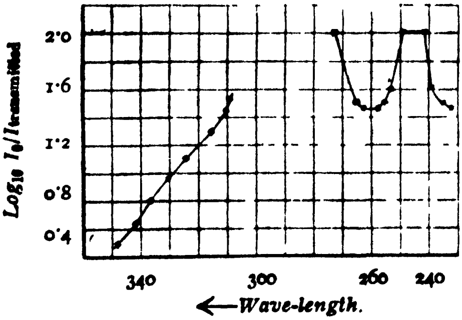


TABLE V.

Absorbing substance.	Mol. extinct. coefficient at 254 $\mu\mu$.	Mol. extinct. coefficient at 366 $\mu\mu$.
Ferric hydroxide sol	10,747	5,373
Methylene blue	23,485	2,500

Effect of Varying the Intensity of Absorbed Radiation.

TABLE VI.

Temp. $=29^0$. $p_H = 4{\cdot}8$. $d = 0{\cdot}5$ cm.

Wave-length	Conc. of sol.	Reductant.	Conc. of Me blue. $\times 10^6$	I_{abs} (mix).	$K \times 10^{12}$.
		Glucose.			
(a) 366 $\mu\mu$	0.0107M	1%	50·0M	2544	3·55
,,	,,	,,	,,	1681	2·39
		Laevulose.			
(b) 366 $\mu\mu$	0·0107M	0·25%	50·0	2163	9·93
,,	,,	,,	,,	1542	7·48

The velocity constant varies directly as the intensity of radiation absorbed.

Quantum Efficiency of the Process.

As in Part XIII, the fraction of the radiation absorbed by the sol alone was taken into consideration while calculating the quantum efficiencies of these photochemical reactions and calculated by the equation (A).

In this case, the concentration of methylene blue being relatively very small and the molecular extinction coefficient of methylene blue and ferric hydroxide sol being of the same order, practically the whole of the absorbed light was absorbed by the sol. The quantum efficiency (γ) was much less than unity (*vide* Table II)

Temperature Coefficient of the Reaction.—The temperature coefficient is small being of the order of 1.1—1.2.

Influence of Polarised Light.

TABLE VII.

Wave-length = 366 $\mu\mu$. Temp. = 29°. p_H = 4·8. Sol = 0·0107M. Methylene blue = 50·0 × $10^{-6}M$. Glucose = 1%.

	Nature of light.	$I_{abs.}$	$K \times 10^{18}$.
(a)	Ordinary	2492	3·48
(b)	*d*-Circularly polarised (reaction mixture not pre-exposed to sunlight).	,,	0·93
(c)	*l*-Circularly polarised (reaction mixture not pre-exposed to sunlight).	,,	1·02

In the last two cases (c and d) induction period was about 14 hours. Now from the above table we see that $V_l > V_D$, the terms having the usual significance.

DISCUSSION.

Any mechanism of reaction that may be proposed should be in a position to explain the following facts:—

(1) The velocity of reaction with respect to methylene blue is zero-molecular.

(2) The reactions are attended with long induction periods.

(3) Upto a certain concentration of reductants, the velocity constant undergoes no change with change in concentration of reductant. Below this limiting concentration of reductants, the velocity constant diminishes with the decrease in the concentration of reductant and $1/C$ plotted against $1/K$ gives a straight line.

(4) The velocity constant diminishes slightly with diminishing concentration of sol, the intensity of absorbed radiation diminishing slightly.

(5) The constant passes through a maximum at p_H 4·8 to almost zero as the p_H of the reacting system diminishes.

(6) The velocity constant varies directly as the intensity of absorbed radiation

(7) Temperature coefficient is small.

(8) The quantum efficiency which is very much less than unity, has almost the same value at 254$\mu\mu$ and 366$\mu\mu$.

The sol surface is completely covered with a unimolecular layer of the dye-molecule even at very low concentration of the dye. It is remarkable that the absorption of radiation by the dye-molecules directly does not lead to the photoreduction by reaction with reductant. But a dye-molecule can be brought into activated state by receiving energy from the elementary spaces of the ferric hydroxide sol surface which is also excited by the absorption of radiation.

The low quantum efficiency can be due to two reasons:—

(*a*) Only a small fraction of the radiation absorbed by the sol is available for the activation of the dye-molecules on the surface of the sol or

(*b*) the velocity of reaction between activated molecules and the reductant adsorbed on the surface of the sol is so slow that most of the former revert spontaneously to the normal state. It is difficult to decide between these two possibilities.

The velocity is given by

$$\frac{dx}{dt} = K'.\frac{\text{I}}{Nh\nu}.C^s_s = K \qquad \ldots \quad (i)$$

where C^s_s is the surface concentration of the reductant.

According to Langmuir

$$C^s_s = \frac{K_1 C^s_s}{K_3 + K_2 C^s_s} \qquad \ldots \quad (ii)$$

where C^s_s is the concentration of reductant in solution.

When C^s_s is very large, $K_3 + K_2 C^s_s$ may be taken as equal to C^s_s

$$\text{or} \quad \frac{dx}{dt} = K = \frac{K_1}{K_2} \qquad \ldots \quad (iii)$$

That is, the velocity constant is independent of reductant concentration when the latter is high as has been experimentally found to be the case.

At a lower concentration of reductant K_3 can not be neglected in comparison to K_2 C^s_s.

$$\text{Hence} \quad \text{I}/K = K_4.\frac{K_3 + K_1 C^s_s}{K_2 C^s_s}$$

$$= \frac{K_5}{C^s_s} + K_4 \qquad \ldots \quad (vi)$$

That is at low concentration of reductant, I/K plotted against, C^s_s should give a straight line. This has been experimentally realised.

The velocity of reaction has been found to be proportional to the intensity of absorbed radiation as is demanded by equation (*i*).

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PHOTOCHEMICAL REACTION WITH SOME INORGANIC COLLOIDS AS ACTIVE AGENTS UNDER THE INFLUENCE OF LIGHT IN VARIOUS STATES OF POLARISATION. PART XIII. INFLUENCE OF THE STATE OF POLARISATION OF LIGHT ON THE VELOCITY OF PHOTO-OXIDATION OF ORGANIC SUBSTANCES BY HYDROGEN PEROXIDE WITH COLLOIDS AS PHOTOSENSITISERS.

By Tarapada Banerjee.

In this part results on the influence of polarised light in bringing about photo-oxidations of organic substances by hydrogen peroxide with inorganic colloids as photosensitisers have been given. Colloids used are (*i*) tungstic acid sol, (*ii*) molybdic acid sol, (*iii*) vanadic acid sol, (*iv*) chromic tungstate sol, and (*v*) chromic hydroxide sol.

The kinetics of these reactions in unpolarised light have been studied in detail (*cf.* Banerjee, *J. Indian Chem. Soc.*, 1937, **14**, 59). The experimental procedure and arrangement have been described in Part I of this series (*J. Indian Chem. Soc.*, 1937, **14**, 495).

In the present case the reacting systems, immediately after mixing the reagents, were exposed to radiation (366$\mu\mu$) in either *d*- or *l*-circularly polarised state. The velocity of reaction was measured after the induction period was over. The induction period of these photo-oxidations in the circularly polarised light varied from 6 to 8 hours.

Photochemical Oxidation of Organic Substances by Hydrogen Peroxide with Tungstic Acid Sol as Photosensitiser (with or without promoters).

When the concentration of hydrogen peroxide was 0·02*M*, which is the concentration of hydrogen peroxide at which reactions described in the present paper are given, the reaction was found to obey unimolecular law.

The concentration of tungstic acid sol (in terms of tungstate equivalent) was 0·025*M*. The velocity of reaction varied as the square root of absorbed radiation.

TABLE I.

Composition of reaction mixture:—sodium tungstate $=0{\cdot}025M$; $H_2O_2=0{\cdot}02M$; glucose $=0{\cdot}025M$; $HCl=0{\cdot}08N$. Temp. $=30°$. $\lambda=366\mu\mu$. I_{abs} = Intensity of light absorbed in ergs per cm²/sec.

	Unpolarised.	*l*-Circularly polarised.	*d*-Circularly polarised.
I_{abs} ..	383	728	728
$K_{unimol}\times 10^5$ ...	3·91	5·68	4·21

TABLE II A.

Formaldehyde as reductant.

$\lambda=366\mu\mu$. Temp $=30°$. Tungstate $=0{\cdot}025M$. $H_2O_2=0{\cdot}02M$. $H{\cdot}CHO=0{\cdot}036M$. $HCl=0{\cdot}0877N$.

Nature of light used.	I_{abs}.	$K_{unimol}\times 10^5$.
Unpolarised	1931	2·88
l-Circularly polarised	158	0·79
d- „ polarised	158	0·61

TABLE II B.

Laevulose as reductant.

Laevulose $=0{\cdot}025M$. $HCl=0{\cdot}078N$. Other factors same as in Table IIA.

Nature of light used.	I_{abs}.	$K_{unimol}\times 10^5$.
Unpolarised	1931	6·97
l-Circularly polarised	241	2·23
d-Circularly polarised	241	1·98

TABLE III.

Glucose as reductant (in presence of promoters).

$\lambda = 366\mu\mu$. Temp. $= 31°$. Glucose $= 0{\cdot}025M$. Tungstate $= 0{\cdot}025M$.

Nature of light.	I_{abs}.	$K_{unimol} \times 10^5$.	Nature of light.	I_{abs}.	$K_{unimol} \times 10^5$.
(a) Promoter ($M/2500$) – $FeCl_3, 6H_2O$. $H_2O_2 = 0{\cdot}01M$. $HCl = 0{\cdot}08N$.			(b) Promoter ($M/2500$) – $FeCl_3, 6H_2O$. $H_2O_2 = 0{\cdot}0086M$. $HCl = 0{\cdot}08N$		
l-Circularly ploarised	360	4·88	*l*-Circularly polarised	360	4·78
d-Circularly polarised	360	3·91	*d*-Circularly polarised	360	3·68
(c) Promoter ($M/20{,}000$) – $FeSO_4, 7H_2O$. $H_2O_2 = 0{\cdot}0126M$. $HCl = 0{\cdot}1175N$.			(*d*) Promotei ($M/20\,000$) $FeSO_4, 7H_2O$. $H_2O_2 = 0{\cdot}0159\ M$. $HCl = 0{\cdot}1175\ N$.		
Unpolarised	2980	15·00			
l-Circularly polarised	600	7·06	*l*-Circularly polarised	600	7·82
d-Circularly polarised	600	5·52	*d*-Circularly polarised	600	6·44

(*e*) Promoter $= M/20{,}000$-$CuSO_4, 7H_2O$. $H_2O_2 = 0{\cdot}0138\ M$. $HCl = 0{\cdot}1175\ N$.

Unpolarised	2980	15·76
l-Circularly polarised	600	7·13
d-Circularly polarised	600	5·75

From the above tables it is evident $V_0 = V_L > V_D$, the terms having the usual significance.

Photochemical Oxidation of Glucose by Hydrogen Peroxide with Chromic Tungstate Sol as Photosensitiser.

This piece of work was taken to investigate the influence of light of different wave-lengths upon this photo-reaction.

Unpublished data by the author on this reaction at 579 $\mu\mu$ showed that in this case the reaction was always zero-molecular. At 579 $\mu\mu$ the velocity constant varied directly as the intensity of absorbed radiation but at $366\mu\mu$ it varied as the square root of absorbed radiation. The circularly polarised light in two opposite directions was obtained in two ways (*i*) with the help of $\lambda/4$ plate or (*ii*) with the help of Fresnel Rhomb.

TABLE IVA.

Light circularly polarised by $\lambda/4$ plate (as described in Part I).

$\lambda = 579\mu\mu$. Temp. = 29·1°. Glucose = 0·025*M*. HCl = 0·039 *N*. H_2O_2 = 0·0114. Chromic tungstate = 0·0265*M*.

		Unpolarised.	*l*-Circularly polarised.	*d*-Circularly polarised.
I_{abs}	...	2500	1100	1100
$K_0 \times 10^{10}$	...	7·24	3·32	2·56

TABLE IVB.

$\lambda = 366\mu\mu$. Temp. = 30·5°. H_2O_2 = 0·0108*M*, Chromic tungstate = 0·0082*M*. Glucose = 0·025*M*. HCl = 0·039 *N*.

		Unpolarised.	*l*-Circularly polarised.	*d*-Circularly polarised.
I_{abs}	...	505	229	229
$K_{unimol} \times 10^5$	...	2·53	1·69	1·16

Experiments with Fresnel Rhomb.—The experiments at $579\mu\mu$ (*cf.* Table IV A) were repeated with 1000 c.p. point-o-lite lamp and the Fresnel Rhomb.

Description of the Apparatus.—The polariser consisted of a large Nicol which was fitted with a graduated circle and the vernier attached to the larger circle. The Fresnel Rhomb was set up with its face vertical. When the short axis of Nicol was kept vertical, plane polarised light was obtained. For *d*- and *l*-circularly polarised light, the polariser was rotated through 45° from the zero position towards the right and left respectively.

TABLE V.

Region = $579\mu\mu$. Temp. = 30·5°. Glucose = 0·025*M*. Tungstate = 0·0265*M*. H_2O_2 = 0·0096*M*. HCl = 0·04*N*.

Nature of light used.	I_{abs}.	$K_0 \times 10^{10}$.
l Circularly polarised.	930	2·89
d-Circularly polarised.	930	2·11

Thus as before $V_L > V_D$, the terms having the same meaning as before.

Photochemical Oxidation of Glucose by Hydrogen Peroxide in Acid Medium with Vanadic Acid Sol as Photosensitiser.

The reaction followed the zero-molecularlaw with respect to hydrogen peroxide and the velocity constant varied as the square root of the intensity of absorbed radiation.

TABLE VI.

$\lambda = 366\mu\mu$. Temp. = 27°. p_H = 5·0. Sodium vanadate = 0·033 M. H_2O_2 = 0·01 M. Acetic acid = 0·018 M. Glucose = 0·05 M.

		Unpolarised.	*l*-Circularly polarised.	*d*-Circularly polarised.
I_{abs}	...	1256	307	307
$K_0 \times 10^{10}$	...	5·17	2·56	1·96

From the above table, it is evident that $V_0 = V_L > V_D$, the terms having the usual significance.

Photochemical Oxidation of Glucose by Hydrogen Peroxide at p_H 5·2 with Chromic Hydroxide Sol as Photosensitiser.

The reaction was unimolecular with respect to hydrogen peroxide.

TABLE VII.

Region = $579\mu\mu$. Temp. = 28°. Glucose = 0·025 M. H_2O_2 = 0·0157 M. Chromic hydroxide = 0·02105 M.

Nature of light used.	I_{abs}.	K_{unimol} with respect to H_2O_2.
l-Circularly polarised	229	$3{\cdot}56 \times 10^{-6}$.
d-Circularly polarised	229	$3{\cdot}56 \times 10^{-6}$

From the above table it is evident that $V_L = V_D$, the terms having the usual significance.

Photochemical Oxidation of Glucose by Hydrogen Peroxide in presence of Molybdic Acid Sol as Photosensitiser.

After the induction period was over, the reaction was always zero-molecular. The velocity constant was directly proportional to the intensity of absorbed radiation.

TABLE VIII.

$\lambda = 366 \mu\mu$. Temp. $= 31°$. Alcohol $= 4.346M$. HCl $= 0.0746N$. Molybdate $= 0.05M$. $H_2O_2 = 0.022M$

	Unpolarised	*l*-Circularly polarised.	*d*-Circularly polarised
I_{abs} ...	1635	252	252
$K \times 10^{10}$ ...	10·79	1·76	1·76

From the above table it is evident that $V_0 = V_l = V_D$, the terms having the same significance as before.

From Tables I-VI it is quite evident that under otherwise identical conditions *l*-circularly polarised light is more efficient than *d*-circularly polarised light in bringing about photochemical oxidation with tungstic acid, chromic tungstate and vanadic acid sols as photosensitisers, while in presence of molybdic acid sol and chromic hydroxide sol, light in the two states of circular polarisation is equally efficient.

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PHOTOCHEMICAL REACTION WITH SOME INORGANIC COLLOIDS AS ACTIVE AGENTS UNDER THE INFLUENCE OF LIGHT IN VARIOUS STATES OF POLARISATION PART XIV. INFLUENCE OF CIRCULARLY POLARISED LIGHT ON PHOTOCHEMICAL REACTIONS WITH PRE-EXCITED COLLOIDS AS PHOTOSENSITISERS.

By J. C. Ghosh and T. Banerjee.

Section A.

In the previous papers of this series, it was observed that the photochemical reactions, which we have studied, are characterised by a considerable induction period. The reacting systems immediately after mixing up were exposed to radiations in a definite state of polarisation and the reaction velocities under the influence of the same radiation were determined after the induction period was over. It was found that in the case of some photo-active sols the reaction velocities for the same intensities of *l*-circularly polarised radiations were greater than those with the corresponding *d*-circularly polarised light. In this section will be described the results of preliminary experiments which were carried out with sols which were exposed to and matured in light of a definite state of polarisation, before being mixed with the other constituents of the reacting system. It has already been shown that if a sol immediately after its preparation is allowed to mature by exposure to radiation for a sufficient length of time and then mixed with the other components of the reaction mixture, the induction period disappears. Such a process we have termed the process of *pre-excitation* and such sols, we shall describe, as *pre-excited* or *pre-activated* sols.

Photochemical Reduction of Tungstic Acid Sol by Glucose (Ref. Part II ; *this Journal*, 1937, p. 519)

TABLE I.

Tungstate = 0·025*M*. Glucose = 10%. p_H = 1·24. Temp. = 29·5°. $\lambda = 366 \mu\mu$. *d*(thickness of the reaction cell) = 0·5 cm. I_{abs} = Intensity of absorbed radiations in ergs/cm^2/sec. γ = Quantum efficiency.

	Sol preactivated in	Reaction carried in	I_{abs} in which the reaction was carried.	$K_0 \times 10^{10}$.	γ.
1.	Ordinary light from point source quartz mercury lamp	Ordinary	146	1·17	1·29
2.	Do	*d*-Circularly polarised	113	0·95	1·38
3.	Do	*l*-Circularly ,,	113	0·95	1·38
4.	*l*-Circularly polarised	*l*-Circularly ,,	113	0·95	1.38
5.	*d*-Circularly ,,	*d*-Circularly ,,	113	0·70	1·01

Photochemical Oxidation of Glucose by Methylene Blue with Ferric Hydroxide Sol as Photosensitiser. (Ref. Part XII, p. 603)

TABLE II.

Sol $= 0·0107M$. Methylene blue $= 50 \times 10^{-6}M$. Glucose $= 1\%$. $p_H = 4·8$. Temp. $= 29°$.

Nature of light in which the		I_{abs} in which the reaction was carried out.	$K_0 \times 10^{13}$.
sol was pre-activated.	reaction was carried.		
Sunlight for 5 mins	Ordinary	2492	3·48
,,	*l*-Circularly polarised	682	1·00
,,	*d*-Circularly polarised	682	0·99

Photochemical Oxidation of Glucose by Hydrogen Peroxide in Acid medium with Tungstic Acid Sol as Photo-catalyst (Banerjee, *J. Indian Chem. Soc.*, 1937, **14**, 59).

TABLE III.

Glucose $= 0·025M$. Tungstate $= 0·025M$. HCl $= 0·08N$. Temp. $= 30°$. $H_2O_2 = 0·015M$.

Sol pre-activated in	Reaction carried in	I_{abs}.	$K_{unimol} \times 10^5$.
(*a*) *l*-Circularly polarised	*l*-Circularly polarised	480	4·49
(*b*) *d*-Circularly polarised	*d*-Circularly polarised	480	3·38
(*c*) Ordinary light	*d*-Circularly polarised	58	1·56
Do	*l*-Circularly polarised	58	1·56

Photochemical Oxidation of Glucose by Hydrogen Peroxide in Acid medium with Vanadic Acid Sol as Photo-catalyst (Banerjee, *loc. cit.*).

TABLE IV.

Glucose $=0\cdot05M$. Vanadate $=0\cdot033M$. Acetic acid $=0\cdot018\,M$. $H_2O_2=0\cdot01M$.
$p_H=5\cdot0$. $\lambda=366\mu\mu$. Temp. $=27°$.

Sol pre-excited in	Reaction carried in	I_{abs} in which the reaction was carried out.	$K_0\times10^{10}$.
Ordinary light	*l*-Circularly polarised	526	3·53
,,	*d*-Circularly polarised	,,	3·45
l-Circularly polarised	*l*-Circularly polarised	,,	3·39
d-Circularly polarised	*d*-Circularly polarised	,,	2·37

Tables (I—IV) show that *l*-circularly polarised light is under otherwise identical conditions, more efficient than *d*-circularly polarised light, only when light in which the sol is pre-excited and light in which the reaction is carried out is in the same state of circular polarisation.

SECTION B.

Summary of the results on differences in velocities of many photochemical reactions which were observed with the same intensities of light in the two opposite states of circular polarisation, are given in Tables VA, VB, VC, VI and VII. V_l and V_D represent the velocity constants in *l* and *d*-circularly polarised light respectively, I_L, and I_D being the corresponding intensities of absorbed radiation. It should be noted that in these cases, illumination during the long induction period was effected by the same polarised beam which was responsible for the later photochemical action.

In Table VII, V_{OL} represents velocity constant in *l*-circularly polarised light with sol pre-excited in ordinary light, V_{OD}, that in *d*-circularly polarised light with sol pre-activated in *l*-circularly polarised light, V_{LL}, that in *l*-circularly polarised light with sol pre-excited in *l*-circularly polarised light, V_{DD}, that in *d*-circularly polarised light with sol pre-excited in *d*-circularly polarised light, I_{OL}, I_{OD}, I_{LL}, and I_{DD} being the corresponding intensities of absorbed radiation.

TABLE VA.

General observation—$V_L > V_D$.

The velocity of reaction varies directly as the intensity of absorbed radiation and was calculated after the induction period was over.

(1) Serial No.	(2) Ref. to part of this series.	(3) Comp. of reaction mixture.	(4) V_L / I_L.	(5) V_D / I_D.
1.	II	Tungstic acid + HCHO	$\frac{1\cdot 39\times 10^{-10}}{237} = 5\cdot 86\times 10^{-13}$	$\frac{0\cdot 95\times 10^{-10}}{237} = 4\cdot 00\times 10^{-13}$
2.	II	Tungstic acid + glucose	$\frac{0\cdot 70\times 10^{-10}}{237} = 2\cdot 95\times 10^{-13}$	$\frac{0\cdot 40\times 10^{-10}}{237} = 1\cdot 69\times 10^{-13}$
3.	II	Tungstic acid + Laevulose	$\frac{0\cdot 61\times 10^{-10}}{180} = 3\cdot 39\times 10^{-13}$	$\frac{0\cdot 40\times 10^{-10}}{180} = 2\cdot 22\times 10^{-13}$
4.	II	Tungstic acid + lactic acid	$\frac{1\cdot 87\times 10^{-10}}{195} = 9\cdot 59\times 10^{-13}$	$\frac{1\cdot 28\times 10^{-10}}{195} = 6\cdot 56\times 10^{-13}$
5.	II	Tungstic acid + mandelic acid	$\frac{1\cdot 22\times 10^{-10}}{328} = 3\cdot 71\times 10^{-13}$	$\frac{0\cdot 87\times 10^{-10}}{328} = 2\cdot 65\times 10^{-13}$
6	II	Tungstic acid + leucine	$\frac{0\cdot 79\times 10^{-10}}{385} = 2\cdot 05\times 10^{-13}$	$\frac{0\cdot 67\times 10^{-10}}{385} = 1\cdot 74\times 10^{-13}$
7.	II	Tungstic acid + Na-hypophosphite	$\frac{1\cdot 54\times 10^{-10}}{192} = 8\cdot 02\times 10^{-13}$	$\frac{1\cdot 34\times 10^{-10}}{192} = 6\cdot 97\times 10^{-13}$

TABLE VA (*contd.*).

(1)	(2)	(3)	(4)	(5)
	X	Tungstic acid + K-indigo-tetrasulphonate + glucose	$\frac{0{\cdot}302 \times 10^{-7}}{1030} = 2{\cdot}93 \times 10^{-11}$	$\frac{0{\cdot}197 \times 10^{-7}}{1030} = 1{\cdot}91 \times 10^{-11}$
	XII	Ferric hydroxide sol + methylene blue + glucose	$\frac{1{\cdot}02 \times 10^{-12}}{682} = 1{\cdot}49 \times 10^{-15}$	$\frac{0{\cdot}93 \times 10^{-12}}{682} = 1{\cdot}36 \times 10^{-15}$
10.	(Banerjee, *loc. cit.*)	Chromic tungstate + glucose + H_2O_2 (with $\lambda/4$ plate)	$\frac{3{\cdot}32 \times 10^{-10}}{1100} = 3{\cdot}02 \times 10^{-13}$	$\frac{2{\cdot}56 \times 10^{-10}}{1100} = 2{\cdot}33 \times 10^{-13}$
		Do (with Fresnel Rhomb)	$\frac{2{\cdot}89 \times 10^{-10}}{930} = 3{\cdot}11 \times 10^{-13}$	$\frac{2{\cdot}11 \times 10^{-10}}{930} = 2{\cdot}27 \times 10^{-13}$

TABLE VB.

General observation — $V_L > V_D$.

The velocity of reaction varies as the square root of absorbed radiation and was recorded after the induction period was over.

Serial No.	Ref. to Part of this series	Comp. of the reaction mixture.	V_L / I_L .	V_D / I_D.
(1)	(2)	(3)	(4)	(5)
1.	IX	Tungstic acid + alcohol + iodine	$\frac{1{\cdot}36 \times 10^{-10}}{\sqrt{310}} = 7{\cdot}71 \times 10^{-12}$	$\frac{1{\cdot}05 \times 10^{-10}}{\sqrt{310}} = 5{\cdot}96 \times 10^{-12}$
2.	IX	Tungstic acid + glucose + iodine	$\frac{2{\cdot}05 \times 10^{-10}}{\sqrt{570}}$ $8{\cdot}59 \times 10^{-12}$	$\frac{1{\cdot}74 \times 10^{-10}}{\sqrt{570}}$ $7{\cdot}29 \times 10^{-12}$

TABLE VB (*contd.*).

(1)	(2)	(3)	(5)	(4)
3.	Banerjee (*loc. cit.*)	Tungstic acid + glucose + H_2O_2	$\frac{5{\cdot}68\times10^{-5}}{\sqrt{728}} = 2{\cdot}11\times10^{-6}$	$\frac{4{\cdot}21\ \ 10^{-5}}{\sqrt{728}} = 1{\cdot}56\times10^{-6}$
4.	,,	Tungstic acid + formaldehyde + H_2O_2	$\frac{0{\cdot}79\times10^{-5}}{\sqrt{158}} = 6{\cdot}29\times10^{-7}$	$\frac{0{\cdot}61\times10^{-5}}{\sqrt{158}} = 4{\cdot}85\times10^{-7}$
5.	,,	Tungstic acid + laevulose + H_2O_2	$\frac{2{\cdot}23\times10^{-5}}{\sqrt{241}} = 1{\cdot}44\times10^{-6}$	$\frac{1{\cdot}98\times10^{-5}}{\sqrt{241}} = 1{\cdot}28\times10^{-6}$
6.	,,	Tungstic acid + glucose + H_2O_2 (in presence of $FeCl_3$, $6H_2O$)	$\frac{4{\cdot}88\times10^{-5}}{\sqrt{360}} = 2{\cdot}57\times10^{-6}$	$\frac{3{\cdot}91\times10^{-5}}{\sqrt{360}} = 3{\cdot}06\times10^{-6}$
7.	,,	Tungstic acid + glucose + H_2O_2 (in presence of $FeSO_4$, $7H_2O$)	$\frac{7{\cdot}06\times10^{-5}}{\sqrt{600}} = 2{\cdot}88\times10^{-6}$	$\frac{5{\cdot}52\times10^{-5}}{\sqrt{600}} = 2{\cdot}25\times10^{-6}$
8.	,,	Tungstic acid + glucose + H_2O_2 (in presence of $CuSO_4$, $7H_2O$)	$\frac{7{\cdot}13\times10^{-5}}{\sqrt{600}} = 2{\cdot}91\times10^{-6}$,	$\frac{5{\cdot}75\times10^{-5}}{\sqrt{600}} = 2{\cdot}35\times10^{-6}$
9.	,,	Chromic tungstate + glucose + H_2O_2 at 366$\mu\mu$	$\frac{1{\cdot}69\times10^{-5}}{\sqrt{229}} = 1{\cdot}41\times10^{-6}$	$\frac{1{\cdot}16\times10^{-5}}{\sqrt{229}} = 7{\cdot}68\times10^{-7}$
10.	,,	Vanadic acid sol (from acetic acid) + glucose + H_2O_2	$\frac{2{\cdot}56\times10^{-10}}{\sqrt{307}} = 1{\cdot}46\times10^{-11}$	$\frac{1{\cdot}96\times10^{-10}}{\sqrt{307}} = 1{\cdot}12\times10^{-11}$

TABLE Vc.

Observation—$V_L > V_D$.

The velocity constant is neither proportional to the intensity of absorbed radiation nor to the square root of absorbed radiation.

Serial No. (1)	Ref. to Part of this series. (2)	Comp. of the reaction mixture. (3)	V_L / I_L. (4)	V_L / I_D. (5)
1	IV	Vanadic acid sol (from HCl) + alcohol	$\frac{0{\cdot}90 \times 10^{-10}}{560} = 1{\cdot}61 \times 10^{-13}$	$\frac{0{\cdot}58 \times 10^{-10}}{560} = 1{\cdot}04 \times 10^{-13}$

TABLE VI.

General observation—$V_L = V_D$.

The velocity of reaction is proportional to intensity of radiation absorbed.

(1)	(2)	(3)	(4)	(5)
1	IV	Molybdic acid + HCHO	$\frac{0{\cdot}067 \times 10^{-9}}{76{\cdot}8} = 8{\cdot}72 \times 10^{-13}$	$\frac{0{\cdot}066 \times 10^{-9}}{76{\cdot}8} = 8{\cdot}59 \times 10^{-13}$
2	IV	Molybdic acid + glucose	$\frac{0{\cdot}052 \times 10^{-9}}{76{\cdot}8} = 6{\cdot}70 \times 10^{-13}$	$\frac{0{\cdot}051 \times 10^{-9}}{76{\cdot}8} = 6{\cdot}64 \times 10^{-13}$
3	IV	Molybdic acid + alcohol	$\frac{0{\cdot}018 \times 10^{-9}}{109{\cdot}8} = 1{\cdot}64 \times 10^{-13}$	$\frac{0{\cdot}017 \times 10^{-9}}{109{\cdot}8} = 1{\cdot}55 \times 10^{-13}$

TABLE VI (*contd.*).

(1)	(2)	(3)	(4)	(5)
4	IV	Molybdic acid + leucine	$\frac{0{\cdot}118\times10^{-9}}{433}=2{\cdot}73\times10^{-13}$	$\frac{0{\cdot}116\times10^{-9}}{433}=2{\cdot}68\times10^{-13}$
5	VII	Uranic acid sol + sodium tartrate	$\frac{0{\cdot}157\times10^{-6}}{300}=5{\cdot}23\times10^{-10}$	$\frac{0{\cdot}165\times10^{-6}}{300}=5{\cdot}5\times10^{-10}$
6	XI	Uranic acid sol + glucose + methylene blue	$\frac{0{\cdot}350\times10^{-10}}{220}=1{\cdot}59\times10^{-13}$	$\frac{0{\cdot}350\times010^{-10}}{220}=1{\cdot}59\times10^{-13}$
7	Banerjee (*loc. cit.*)	Chromic hydroxide + glucose + H_2O_2	$\frac{3{\cdot}65\times10^{-5}}{229}=1{\cdot}59\times10^{-7}$	$\frac{3{\cdot}56\times10^{-5}}{229}=1{\cdot}55\times10^{-7}$
8	,,	Molybdic acid sol + ethyl alcohol + H_2O_2	$\frac{1{\cdot}76\times10^{-10}}{252{\cdot}4}=0{\cdot}69\times10^{-12}$	$\frac{1{\cdot}76\times10^{-10}}{252{\cdot}4}=0{\cdot}69\times10^{-12}$

TABLE VII.

Serial No. (1)	Ref. to Part of this series. (2)	Comp. of reaction mixture. (3)	V_{OD}/I_{OD} (4)	V_{OI}/I_{OI}. (5)	V_{DD}/I_{DD}. (6)	V_{LL}/I_{LL}. (7)
1.	II	Tungstic acid + glucose	$\frac{0{\cdot}95\times10^{-10}}{113}=0{\cdot}84\times10^{-12}$	$\frac{0{\cdot}95\times10^{-10}}{113}=0{\cdot}84\times10^{-12}$	$\frac{0{\cdot}70\times10^{-10}}{113}=0{\cdot}62\times10^{-12}$	$\frac{0{\cdot}95\times10^{-10}}{113}=0{\cdot}84\times10^{-12}$

TABLE VII (*contd.*).

(1)	(2)	(3)	(4)	(5)	(6)	(7)
2.	XII	Ferric hydroxide + Me-blue + glucose	$\frac{0·99 \times 10^{-10}}{682} = 0·145 \times 10^{-14}$	$\frac{1·00 \times 10^{-10}}{682} = 0·147 \times 10^{14}$	...	...
3.	Banerjee (*loc. cit.*)	Tungstic acid + glucose + H_2O_2	$\frac{1·56 \times 10^{-5}}{\sqrt{58}} = 0·206 \times 10^{-5}$	$\frac{1·56 \times 10^{-5}}{\sqrt{58}} = 0·206 \times 10^{-5}$	$\frac{3·38 \times 10^{-5}}{\sqrt{480}} = 0·154 \times 10^{-5}$	$\frac{4·49 \times 10^{-5}}{\sqrt{480}} = 0·204 \times 10^{-5}$
4.	"	Vanadic acid + alcohol + H_2O_2	$\frac{3·45 \times 10^{-10}}{\sqrt{526}} = 0·15 \times 10^{-10}$	$\frac{3·53 \times 10^{-10}}{\sqrt{526}} = 0·154 \times 10^{-10}$	$\frac{2·37 \times 10^{-10}}{\sqrt{526}} = 0·103 \times 10^{-10}$	$\frac{3·39 \times 10^{-10}}{\sqrt{526}} = 0·147 \times 10^{-10}$

A few important conclusions may be drawn as a result of these investigations on the photochemical activity of sols.

The following sols did not exhibit any circular dichroism when they were exposed to *d*- or *l*-circularly polarised radiations which they are capable of absorbing during the process of aggregation of constituent molecules and ions, to form micelles :—

Molybdic acid, uranic acid and chromic hydroxide. Exposure of photo-active systems containing these sols to *d*- or *l*-circularly polarised light of the same intensity, gave velocity constants of chemical reactions which are always the same.

Sols of tungstic acid, chromic tungstate and vanadic acid behave differently. They do not exhibit circular dichroism when during aggregate formation they are subjected to unpolarised radiation which they can absorb; but when they are exposed to *d*- or *l*-circularly polarised light during aggregate formation, they show pronounced circular dichroism. These are also the sols, which under certain conditions show differential velocities for the same intensity of oppositely circularly polarised radiation, when they form part of a photo-active system. The photosensitive micelles may be formed in (*a*) the reaction mixture containing the sol forming constituents by absorption of radiation during the long period of induction, or in (*b*) the pure sol by long exposure to similar radiations. The pre-activated sol formed in the latter case, does not show any induction period when they form part of a reacting photochemical system. If during the induction period or the process of pre-activation, the system is exposed to unpolarised radiations, and then for chemical reaction, it is exposed to *d*- or *l*- circularly polarised light, no differential velocity of reaction is observed. But if the system is exposed to *d*- or *l*- circularly polarised light during the period of induction or pre-activation, and then the reaction is carried in the same circularly polarised light, it is observed that the velocities are greater for *l*-circularly polarlsed light than for *d*-circularly polarised light. The sol systems which show this differential effect are known to contain particles which are microcrystalline in structure. It is probable. that circularly polarlsed light exercises a directive influence during the process of formation of these microcrystaline photo-active aggregates, and develops an anisotropic lattice structure. This anisotropy manifests itself as circular dichroism and as a differential velocity effect in photochemical reactions under the influence of circularly polarised radiations. When nonpolarised light is used for the development of photo-active aggregates, neither circular dichroism, nor its differential velocity effect is observed, which indicates that the microcrystalline patterns formed under such conditions are isotropic.

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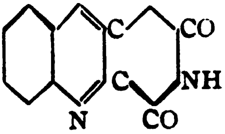
SYNTHESIS IN THE ALLOXAZINE, *ISO*ALLOXAZINE (FLAVIN) AND LUMAZINE GROUPS. PART I.

SYNTHESIS OF 6- OR 7-PHENYL AND 6:7-DIPHENYLLUMAZINES.

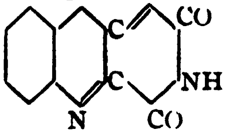
BY K. GANAPATI.

In connection with the investigations on the chemeotherapy of tuberculosis, the author required a group of compounds which can stain the tubercle bacilli and also possess some specific properties so that their metallic salts can be used for intraperitoneal injections. Compounds of the alloxazine (I*a*) and *iso*alloxazine (I*b*) groups, the ring structure of which has recently been shown by Kuhn, Karrer and others to be present in vitamin B_2 (lactoflavin), possess most of the requisite properties (*cf*. Kuhn and Boulanger, *Z. physiol. Chem.*, 1936, **241**, 233). A series of synthetic attempts have, therefore, been launched with a view to synthesise compounds of these groups, with suitable substituents in the benzene ring, which are expected to possess some specific bactericidal effects.

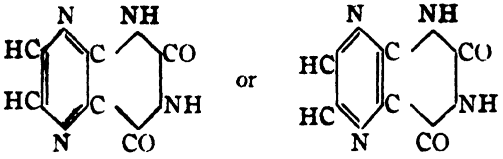
Attempts in introducing particular substituents *e.g.*, I, OH, OR, SH, SR., etc., in the benzene ring of alloxazine or *iso*alloxazine according to the current methods of Kuhn (*Ber.* 1934, **67**, 1459 and following papers; Kühling, *Ber.*, 1891, **24**, 2363) or Karrer (*Helv. Chim. Acta*, 1934, **17**, 1516, and following papers) were attended with working difficulties, since either the requisite substituted diamines were not easily accessible or the corresponding *ortho*nitrohalogen compounds could not be employed. The synthesis of some derivatives of lumazine (II, Kuhn and Cook, *Ber.*, 1937, **70**, 761), with substituents in positions 6 or 7 or both, was next undertaken with a view (*a*) to test whether the phenyl- substituted compounds possess properties (physical and physiological) similar to the alloxazines and (*b*) to elucidate whether the particular properties of the alloxazines are due only to the lumazine residue itself.



(I*a*)



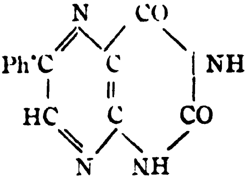
(I*b*)



(II)

Sachs and Meyerheim (*Ber.*, 1908, 41, 3965) condensed 3-methyl-4:5-diaminouracil and also 1:3-dimethyl-4:5-diaminouracil with diacetyl, pyruvic acid and mesoxalic acid and obtained the corresponding lumazine derivatives. Very recently Kuhn and Cook (*loc. cit.*) have obtained the corresponding lumazine derivatives by condensing 4:5-diaminouracil sulphate with diacetyl-glyoxal (polymer), methylglyoxal, β-naphthoquinone and phenanthrene-quinone. Some more new compounds of the above type have now been prepared by condensing 4 : 5-diaminouracil sulphate with phenyl-substituted 1:2-diketones.

Phenylglyoxal hydrate ("Organic Synthesis ", XV, p. 67) was found to condense with 4:5-diaminouracil sulphate to give 6- or -7-phenyllumazine (III or IV), resembling alloxazine in its physical properties. The work on the condensation of various derivatives of phenylglyoxal with 4:5-diaminouracil sulphate as also with 4:5-diaminothiouracil is nearing completion and will shortly be communicated.



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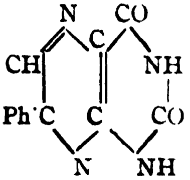

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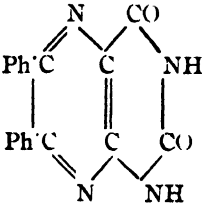
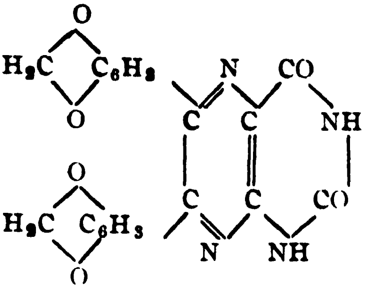


(V)

Benzil condenses with 4:5-diaminouracil sulphate furnishing 6:7-diphenyllumazine (V).

The condensation of 4:5-diaminouracil with a series of mono- and di-substituted benzils did not proceed smoothly; whereas 3:3′-diiodo,- 4:4′-diiodo-, 4:4′-dimethoxy-, 3:3′ -dimethoxy-, and 4-methoxy- benzils appear to yield only traces of products in unworkable yields and benzpiperil did not at all undergo condensation. In the case of the hydroxybenzils, besides bad yields, the working up of the products offered additional difficulties.

Piperil appears to yield the corresponding 6:7-di-(3:4-methylenedioxyphenyl)-lumazine (VI) in bad yield.



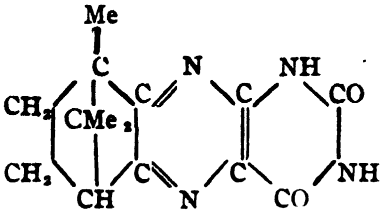
(VI)

Unsuccessful attempts were made to condense phenylglyoxalaldoxime, benzilmonoxime and piperil monoxime with 4-aminouracil to obtain the corresponding lumazines (III or IV), (V) and (VI). Though phenanthrenequinone condenses with 4:5- diaminouracil sulphate to give the corresponding 9′:10′-phenanthrolumazine in very good yield, all attempts to condense phenanthrenequinonemonoxime and 4-aminouracil under a variety of conditions ended in failure.

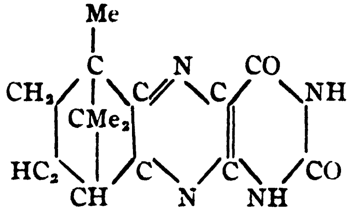
This and the other allied instances clearly show that although the hydrogen atom in position 5 in 4-aminouracil is reactive, yet it does not react with the hydroxyl of the oxime group.

The study of the condensation of 4:5-diaminouracil with the various benzils indicates that the substituteuts in the benzene ring modify the reactivity of the carbonyl groups to a great extent. With a view to find out the individual influences of the various substituents, the condensations with several benzils are being tried It is quite interesting to note that all the benzils (excepting some 2:2′-disubstituted compounds) give the corresponding quinoxaline derivatives with *o*-phenylenediamine (though the dioximes are formed only with difficulty in some cases) which makes it evident that the amino groups in 4:5-diaminouracil are not so reactive as those in *o*-phenylenediamine. It is also significant that phenanthrenequinone condenses with 4:5-diaminouracil quite readily to yield the lumazine in quantitative yields, whereas benzil does not condense so readily and the yield is not so good.

As a preliminary to the study of similar condensations with the 1:2-diketones of the terpene series camphorquinone has been condensed with 4:5-diaminouracil sulphate to yield 2′:3′-camphorolumazine, which can be represented either by (VII) or (VIII).



(VII)



(VIII)

EXPERIMENTAL.

4:5-*Diaminouracil Sulphate.*—This compound was prepared according to the directions of Kuhn and Cook (*loc cit.*) and also by the rapid method of Bogert and Davidson (*J. Amer. Chem. Soc.*, 1933, **55**, 1667). While the former method directly gave a purer product, the latter method gave a better yield and is most suited for large scale preparations, since the conversion of cyanoacetylurea into 4-aminouracil according to the first method could not be effected satisfactorily in quantities more than 4 or 5 g. at a time.

6- *or* 7-*Phenyllumazine.*—In the preparation of phenylglyoxal hydrate, after refluxing acetophenone with selenium dioxide in alcohol for 3 hours, the solvent was removed first under ordinary and then under reduced pressure, and the resulting thick oil being freed from selenium by careful filtration or better by centrifuging, was dissolved in the minimum quantity of boiling water and filtered. On cooling the filtrate, phenylgyoxal hydrate separated in a crystalline form.

A mixture of phenylglyoxal hydrate (0·6 g), 4:5-diaminouracil sulphate (1·0 g.), glacial acetic acid (25 c.c.) and water (175 c.c.) was gently refluxed for 140 minutes when the condensation product separated from the clear solution. After cooling, it was filtered (yield, 0·5 g.) and recrystallised from dilute alcohol when it was obtained as glistening red needles not melting up to 330°. (Found: N, 22·96. $C_{12}H_8O_2N_4$

requires N, 28·33 per cent). Some more of the product could be obtained from the mother liquors on concentration. A dilute alkaline solution of this lumazine shows a green fluorescence.

The dimethyl derivative of the above lumazine was prepared as follows: To the finely powdered lumazine (0·3 g.) was added an ice-cold ethereal solution (40 c.c.) of diazomethane obtained from 1·5 g. of nitrosomethylurea and the mixture allowed to stand for about 20 hours, first few hours being in ice-cold water and then at the room temperature. The ether was removed by distillation and the resulting product crystallised from formic acid. After three crystallisations the methyl derivative was obtained as yellow needles or prisms, m.p. 278°. (Found: N, 21·20. $C_{14}H_{12}O_2N_4$ requires N, 20·89 per cent).

6:7-*Diphenylbenzil.*—When a mixture of benzil and 4:5-diaminouracil sulphate was refluxed in glacial acetic acid for 1 hour, the yield of the lumazine was not found to be good. By prolonging the heating for 5-8 hours, the yield was improved and it was considerably improved by the addition of a little boric acid (Kuhn). The following condition has been found to be the best:

A mixture of benzil (0·5 g.), 4:5-diaminouracil sulphate (0·5 g.), water (100 c.c.) and glacial acetic acid (50 c.c.) with a little boric acid was refluxed for 5 hours and on cooling the solution a mixture of some unchanged benzil and 6:7-diphenyllumazine separated, which was collected. The former can be freed from the condensation product either by washing the mixture thoroughly with carbon tetrachloride or by shaking it with dilute sodium hydroxide, filtering and acidifying the filtrate (yield, 0·38 g.). On recrystallisation from dilute acetic acid, it was obtained as colourless shining crystals, m.p. 310-315° depending upon the rate of heating. (Found: N, 17·45. $C_{18}H_{14}O_2N_4$ requires N, 17·72 per cent). It dissolves in dilute sodium hydroxide forming a light yellow solution which shows a green fluorescence.

Piperil.—Piperonyloin was prepared by Perkin (*J. Chem. Soc.*, 1891, **59**, 164) and in trying to oxidise it to piperil by nitric acid he could not obtain piperil. Biltz and Wienands (*Annalen*, 1899, **308**, 11), however, oxidised it by boiling it in an alkaline solution. This method was not found to be satisfactory in working with large quantities. The following method gave a good yield.

A mixture of piperonal (30 g.), ethyl alcohol (80 c.c.), water (20 c.c.) and sodium cyanide (8 g.) was refluxed on the steam-bath for 1½ hours, a further quantity of sodium cyanide (5 g.) added and the mixture refluxed for 1½ hours more. It was allowed to stand at the room temperature till the liquid at the bottom completely solidified. The filtered product was carefully washed with dilute caustic soda and sodium bisulphite solution and finally with water and dried, yield 27 g. A mixture of finely powdered copper sulphate (42 g.), pyridine (40 c.c) and water (16 c.c.) was heated on the steam-bath with shaking and to the clear solution, piperonyloin (25 g.) was added and heating continued with good shaking for 2½-3 hours. After cooling, the solution was diluted, filtered and the piperil, thoroughly washed free from the copper salt, was obtained as fine yellow prisms. Since it is somewhat sparingly soluble in alcohol, it can also be purified by boiling it with a little alcohol twice and filtering. The product thus obtained melted at 170-71°.

Action of Piperil on 4:5-Diaminouracil Sulphate.—The condensation of piperil with diaminouracil sulphate was tried by boiling equimolecular quantities of the components in a solution of (*i*) glacial acetic acid for 2-12 hours, and also in the presence of boric acid and (*ii*) dimethylaniline. By working up in the usual way, a small quantity of a yellow product was obtained, which showed fluorescence in alkaline solution. It crystallised from a large volume of boiling water, not melting up to 330°. (Found: N, 13·72. $C_{20}H_{12}O_6N_4$ requires N, 13·35 per cent).

2′: 3′-Camphorolumazine.—A solution of camphorquinone (0·8 g.) and diaminouracil sulphate (1·1 g.) in water (125 c.c) and glacial acetic acid (50 c.c.) was heated under reflux for about 1 hour. Since nothing separated on cooling the solution was concentrated to a small volume, diluted a little with water and after standing, the separated crystalline product was filtered off. The product was treated with dilute sodium hydroxide and on acidifying the filtrate, the lumazine separated in a crystalline form. It was collected by filtration and crystallised from dilute acetic acid as yellow prisms, not melting up to 320° (Found: N, 19·96. $C_{14}H_{16}O_2N_4$ requires N, 20·58 per cent). It shows fluorescence in dilute alkaline solution.

The author has great pleasure in thanking Dr. P. C. Guha for his keen interest in the progress of this work. He also thanks the authorities of the Lady Tata Memorial Trust for the award of a scholarship which enabled him to undertake this investigation.

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OXIDATION OF HYDROCARBONS IN THE VAPOUR PHASE. PART I. AROMATIC HYDROCARBONS.

By J. K. Chowdhury and M. A. Sahoor

In this laboratory, toluene was oxidised in the vapour phase in the presence of certain vanadium and nickel catalysts when satisfactory yields of benzoic acid and benzaldehyde were obtained (*J. Indian Chem. Soc.*, 1931, **11**, 185). This work has now been extended further to aromatic hydrocarbons with condensed rings such as naphthalene and phenanthrene. The oxidation was carried out in an electrically heated glass tube with primary and secondary air as described in the above paper. The products of combustion were collected in successive water-cooled receivers which were further cooled with ice in the case of highly volatile products.

The following catalysts were used and their preparation is described below :—

(*i*) Vanadium pentoxide, prepared by heating ammonium metavanadate, the oxide being fused and obtained in granular form by crushing and sieving.

(*ii*) Tin vanadate, obtained by slowly adding a dilute solution of stannic chloride to a solution of sodium metavanadate with constant mechanical stirring. A small quantity of asbestos emulsion was added to the vanadium solution when an asbestos support was desired.

(*iii*) Manganese vanadate was prepared in a similar manner, manganese chloride being used in place of stannic chloride. Pumice was often used as a support and was incorporated in the same way as asbestos.

(*iv*) Mixed tin and vanadium oxides were obtained by fusing a mixture of the oxides in molecular proportion and crushing and sieving the mass thus obtained.

(*v*) Mixed nickel and aluminium oxides were obtained by impregnating a mixture of saw dust and aluminium oxide with a solution of nickel nitrate and the mass was carbonised at 800° in hydrogen atmosphere. The product was maintained at a dull red heat in air until all the carbon was burnt off.

The activity of the above catalysts with special reference to the yield of phthalic anhydride from naphthalene and phenanthrene was studied. Variations in the yield of phthalic anhydride were often noticed though the catalyst used and the conditions of the different experiments were not varied. This was overcome by avoiding any disturbance of the catalyst bed between successive experiments conducted with the same catalyst.

Oxidation of Naphthalene.—Unlike toluene, naphthalene did not yield any aldehyde on oxidation, the main products being phthalic and maleic anhydrides accompanied by small amounts of 1:4-naphthaquinone and traces of benzoic acid and naphthol while carbon monoxide and carbon dioxide were the gaseous products. Phthalic and maleic anhydrides were separated by washing with cold water and were estimated by titration.

The first series of experiments were conducted with a view to determine the optimum quantity of air and the rate of its flow. It was found that excess of air fovoured the yield of phthalic acid. As large quantities of heat were evolved in the reaction, the excess of air served to diffuse the heat and prevented abnormal rise of temperature. Variations in the proportion of primary and secondary air did not greatly influence the yield so long as the total volume of air was in sufficient excess. Using the same catalyst, the quantity and proportion of primary and secondary air and the rate of its flow, temperature of the catalyst bed and of the carburettor, the size of the catalyst particles and the catalyst space were varied. Of the different crtalysts, mixed oxides of tin and vanadium (in molecular proportion) and tin vanadate supported asbestos were found to have the greatest activity. Thus a yield of 61·2% phthalic anhydride (calculated on the amount of naphthalene used) was obtained with mixed oxides of tin and vanadium (unsupported) as catalyst under the following conditions:

Diameter of catalyst tube (glass),	1·5 cm.
Catalyst space	6·3 cc.
Air ratio	3 times of the theoretical.
Time of contact	0·32 sec.
Carburettor temperature	172
Temp. of catalyst bed	290°
Naphthalene attacked	59%
Yield of phthalic anhydride	90%.

As lower furnace temperatures, the product became yellow on account of a higher yield of naphthaquinone while with a longer time of contact (5 sec.) and at the same temperature a higher yield of maleic acid (8·2%) was obtained. With a shorter time of contact, the yield of phthalic anhydride was better but a large amount of naphthalene escaped unoxidised Thus under the conditions noted above, only 59% of the naphthalene used was attacked and hence the actual yield of phthalic anhydride obtained was 90% of the theoretical yield. When tin vanadate (unsupported) was used as the catalyst, the maximum yield of phthalic anhydride obtained was 51·2%

calculated on the naphthalene used but when the same catalyst was mounted on asbestos, the yield increased to 60%.

Using manganese vanadate supported on pumice as the catalyst and varying the different conditions, a maximum yield of only 30% of phthalic anhydride and 12% of maleic anhydride could be obtained. Apparently manganese vanadate is more drastic in its action and oxidises phthalic anhydride further to maleic anhydride and carbon dioxide.

It may be observed that the catalysts, mixed oxide of tin and vanadium and tin vanadate-asbestos, were used in 15-20 consecutive runs without any appreciable loss of efficiency. The best yields were obtained in the 3rd to the 10th run.

Oxidation of Phenanthrene.—The principal product phthalic anhydride, obtained in the catalytic oxidation of phenanthrene, was contaminated with traces of maleic anhydride, naphthalic anhydride, quinone and phenanthrol. Unlike liquid phase oxidation which attacks the middle ring and gives diphenic acid, it is the side ring which is succeptible to gaseous phase oxidation. 1:4-Phenanthaquinone was identified by colour reactions, *i.e.*, (*i*)with concentrated sulphuric acid green colour was obtained and (*ii*) with Lanbaheimer colour test which consists in treating acetic acid solution of the quinone with toluene containing thiotoluene. With sulphuric acid bluish green colour is obtained, when shaken with ether, red-violet colour is obtained.

The carburettor temperature was maintained at a higher level and the arm of the carburettor and the exposed portion of the reaction tube were heated by means of nichrom wire to about 350° to prevent any deposition of phenanthrene. Using the tin vanadate-asbestos as the catalyst, a maximum yield of 22·35% phthalic anhydride was obtained under the following conditions.

Diam. of the reaction tube, 1·5 cm.

Catalyst space, 12·5 cc

Air ratio, 3½ times of the theoretical

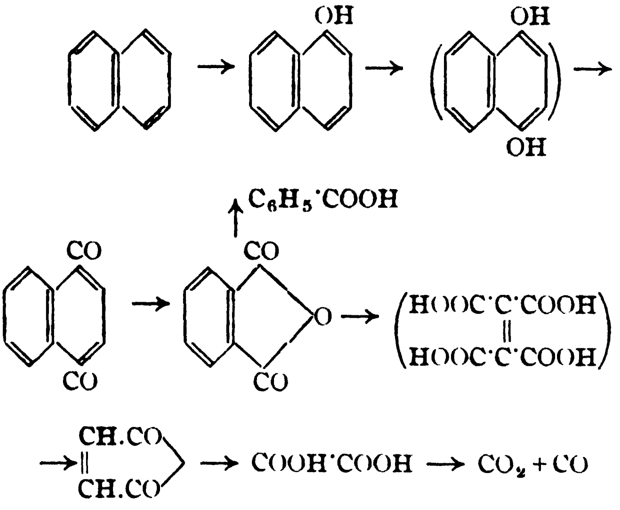
Time of contact, 0·35 sec.

Carburettor temp , 190°

Catalyst temp 420°.

Lower temperatures and shorter time of contact favoured the formation of quinones which turned the product yellow. At higher temperatures, colourless products free from quinones were obtained. As in the case of naphthalene, a large excess of air was necessary to diffuse the heat of the reaction and prevent abnormal rise of temperature. On account of a large number of rings to be opened up, the yield of phthalic anhydride is naturally less than in the case of naphthalene and a large amount of the hydrocarbon is completely burnt off to carbon dioxide. By careful fractional crystallisation of the oxidation products, a beautiful orthorhombic crystalline substance was obtained which from its acid character, m.p. 175° and molecular weight 195·2 (cryoscopic method) was identified as naphthalic anhydride. It was evidently formed by the opening up of the side ring of phenanthrene nucleus.

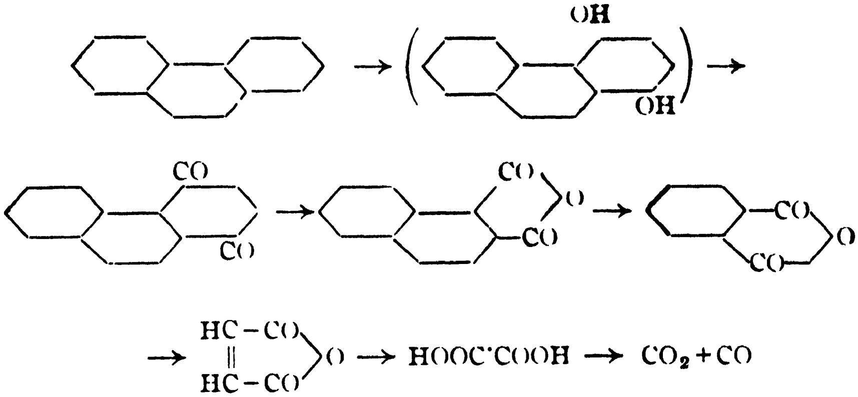
Mechanism of Oxidation.—The formation of the various intermediate products, *i.e.*, traces of naphthol, 1.4-naphthaquinone, phthalic anhydride, benzoic acid and maleic anhydride and carbon dioxide formed in the oxidation of naphthalene may be explained by the following scheme of reactions with the help of the hydroxylation theory of Bone :



It may be observed that only *p*-quinone (1 4) was identified and no other quinone could be detected. It is, therefore, assumed that at high temperatures, hydrogen atoms in *para* position are preferentially hydroxylated.

Before the rupture of the naphthalene nucleus took place only naphthaquinone and minute traces of naphthol were the products that could be detected, the dihydroxy naphthols were extremely susceptible to oxidation and hence their presence could not be detected. No benzene or benzoquinone were found which seems to indicate that phthalic anhydride is directly oxidised to maleic anhydride by the rupture of the benzene nucleus followed by partial decarboxylation and that the oxidation does not proceed through benzene and benzoquinone.

In the case of phenanthrene the course of the oxidation may be represented by the following scheme :—



Before the rupture of the phenanthrene nucleus takes place, phenanthraquinone is obtained by the oxidation of the side ring. This assumption is justified by the fact that no diphenic acid could be detected while naphthalic anhydride was isolated and identified. This may also be explained by the preferential formation of *p*-quinones which is possible only with the side ring. It may be pointed out that the simultaneous oxidation of the two side rings would yield benzene-tetracarboxylic acid whose presence could not, however, be confirmed. It is, therefore, reasonable to assume that once the oxidation begins in a side ring, it travels to the adjoining rings and ruptures them successively before phthalic anhydride is formed.

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OXIDATION OF HYDROCARBONS IN THE VAPOUR PHASE. PART II. HYDROAROMATIC HYDROCARBONS.

By J. K. Chowdhury and M. A. Saboor.

Though hydroaromatic hydrocarbons form an important link between aromatic and aliphatic series, their oxidation does not appear to have received much attention. Jorden (*J. Chem. Met. Soc*. *S. Africa*, 1932, **32**, 248) reported the formation of small amounts of acraldehyde in the vapour phase oxidation of *cyclo*hexane, using manganese vanadate as the catalyst while Yokoyama (*Bull. Chem. Soc Japan*, 1933, **8**, 71) obtained various aliphatic dicarboxylic acids by electrochemical oxidation of *cyclo*hexane at low temperature. Tetrahydronaphthalene was oxidised in the vapour phase by Maxted (*J. Soc. Chem. Ind.*, 1928, 47) and by Green (*ibid.*, 1932, 159T) who obtained good yields of phthalic anhydride and found traces of naphthalene in the oxidation product.

The arrangement described in Part I was used in the oxidation of these hydrocarbons. When the hydrocarbons or their oxidation products were very volatile, the carburettor temperature and the rate of air-flow had to be carefully regulated and the products were cooled with ice-water in two successive coolers and the receiver was covered with wire gauze to avoid any risk from explosion. The uncondensed gases were led through water in succession washers to ensure complete absorption.

Oxidation of cyclo*Hexane*.—The temperature of the catalyst bed was not raised much above 400° on account of the danger of ignition. The condensate was at first light yellow in colour but became cherry red on exposure to air and light, and had an acrolein-like penetrating odour. It responded to tests for aldehydes, acids, unsaturates and peroxides. Amongst aldehydes, acrolein and acetaldehyde and amongst acids, acetic and pyruvic acids were indentified. It may be noted that formic acid, formaldehyde, *cyclo*hexanol and *cyclo*hexane could not be detected The gaseous products of oxidation contained large amounts of carbon monoxide and carbon dioxide. No hydrogen or hydrocarbon was found.

The individual substances in the oxidation product were identified as follows :

(*i*) *Acetaldehyde*.—The liquid condensate was distilled and the presence of acetaldehyde in the distillate was confirmed by (*a*) iodoform test, (*b*)

Nessler's solution and, (*c*) colour test with sodium nitroprusside and piperidine in alkaline solution.

(*ii*) *Acrolein* was detected as a volatile substance having unsaturation and reducing properties and irritating the eyes.

(*iii*) *Acetic acid.*—The distillate was neutralised with sodium bicarbonate, decolourised with a little animal charcoal and the presence of acetic acid was confirmed by the cacodyl oxide test.

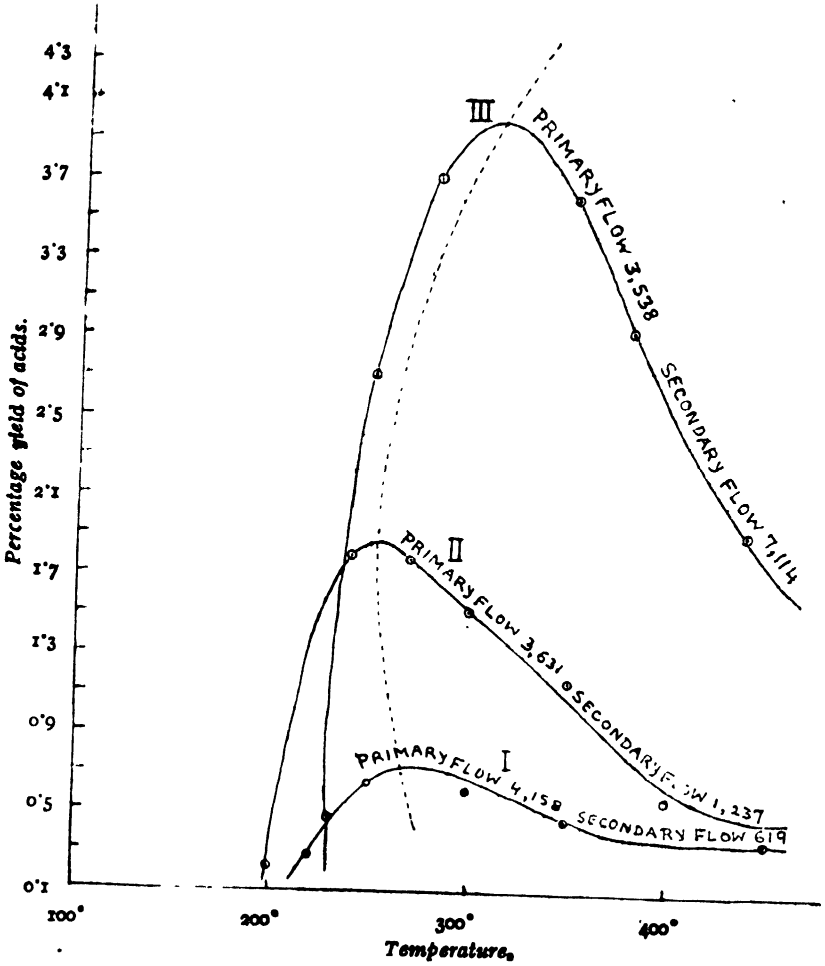
(*iv*) *Pyruvic acid.*—The presence of this acid was unexpected as it escaped the notice of other workers. Its presence in the sodium salts was established by the following tests: (*a*) iodoform test, (*b*) reduction of ammoniacal silver nitrate, (*c*) oxidation by potassium permanganate (*d*) colour test with β-naphthol-sulphuric acid, (*e*) colour test with phloroglucinol-hydrochloric acid and (*f*) evolution of CO_2 by the action of hydrogen peroxide.

(*v*) *Peroxides.*—The presence of peroxides was suspected from a small explosion in the receiver and was indicated by the evolution of iodine from potassium iodide.

The aldehydes were quantitatively estimated by means of sodium bisulphite and are expressed in terms of equivalent iodine, acids by titration in terms of succinic acid and peroxides from the amount of iodine evolved and are expressed in terms of equivalent oxygen.

When tin vanadate was used as the catalyst, the oxidation began at about 200° but at too high a temperature, *i. e.*, above 400° it tended to burn, sometimes with a flame and formed large quantities of carbon dioxide and monoxide, the ultimate products of oxidation. Even at moderate temperature only small amounts of intermediate compounds were obtained, a large portion being completely burnt off. If *cyclo*hexane be passed through the reaction tube, either empty or filled with pumice only, no intermediate product was obtained in appreciable yield, but the introduction of tin vanadate improved the yield of intermediate products and lowered the temperature of reaction. Careful regulation of temperature and introduction of large quantities of air were found to have great influence on the nature and yield of the intermediate products. The curves I, II, and III (Fig. 1) will show how the yield of acids increased with the increase in air supply, the maximum yield being 4% acids (calculated as succinic acid) at a temperature of 310°. Excess of air disseminated the heat of reaction and thus improved the yield of acids. The higher rate of flow of air also shortened the time of contact and thus prevented complete oxidation. It was found that moderate temperatures (250°-340°) favoured the formation of acids and peroxides, while higher temperatures

FIG. 1.



(350°-420°) favoured the formation of aldehydes and unsaturates, the carburettor temperature remaining constant at 25°. This may be due to (1) decomposition of the peroxides at a higher temperature producing aldehydes and (2) preferential combustion of hydrogen in comparison to carbon of the hydrocarbons, thus producing unsaturates.

The peroxide content of the product remained unchanged for about 24 hours but slowly changed on prolonged standing with increase of aldehydes, while the acids remained practically unchanged. The figures in Table I indicate changes in the composition of three separate samples on allowing them to stand in air for three weeks. The increase in aldehyde content may be explained by the decomposition of peroxides of unsaturated hydrocarbons.

TABLE I.

	Sample I.		Sample II.		Sample III.	
	Initial.	Final.	Initial.	Final.	Initial.	Final.
Acids	0·0803	0·0875	0·3259	0·3259	0·2006	0·2019
Aldehydes	0·4666	0·5456	0·2857	0·2903	0·3220	0·3401
Peroxides	0·0866	0·0394	0·0930	0·0462	0·0775	0·0370

Oxidation of Decahydronaphthalene.

The decalin used in these investigations was purified by distillation before use. The general arrangement was the same as in the previous cases and tin vanadate supported on asbestos was mostly used as the catalyst. As in the previous cases, a large excess of air was necessary to dissipate the heat of reaction. The following substances were found in the product of oxidation : phthalic anhydride, maleic anhydride, succinic acid, naphthaquinone, formaldehyde, carbon monoxide and carbon dioxide.

In order to obtain the maximum yield, various conditions such as quantity of air used, the rate of flow, temperature, etc. were varied and a maximum yield of 37·48% phthalic acid was obtained under the following conditions :

Diam. of the reaction tube, 1·5 cm.

Catalyst space, 12 c.c.

Air ratio, 3 times of the theoretical

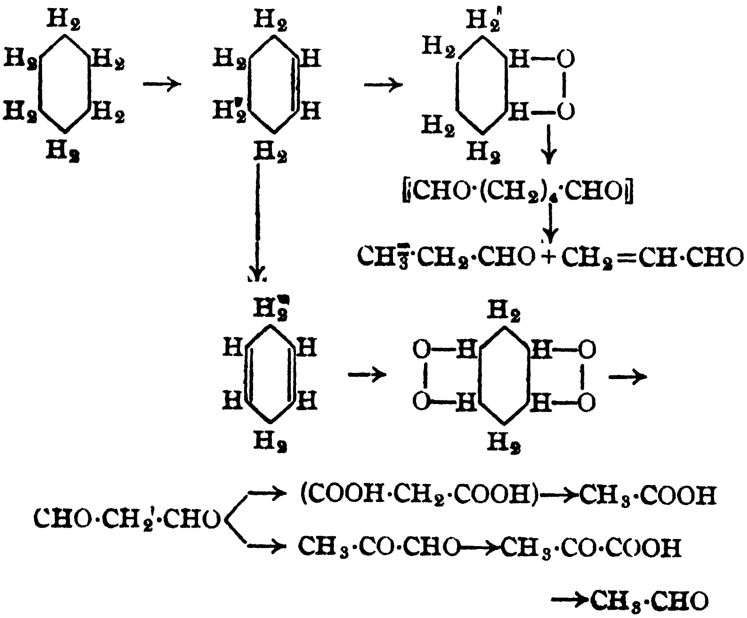
Time of contact, 0·32 sec.

Catalyst temp., 320°.

Carburettor temp., 80°.

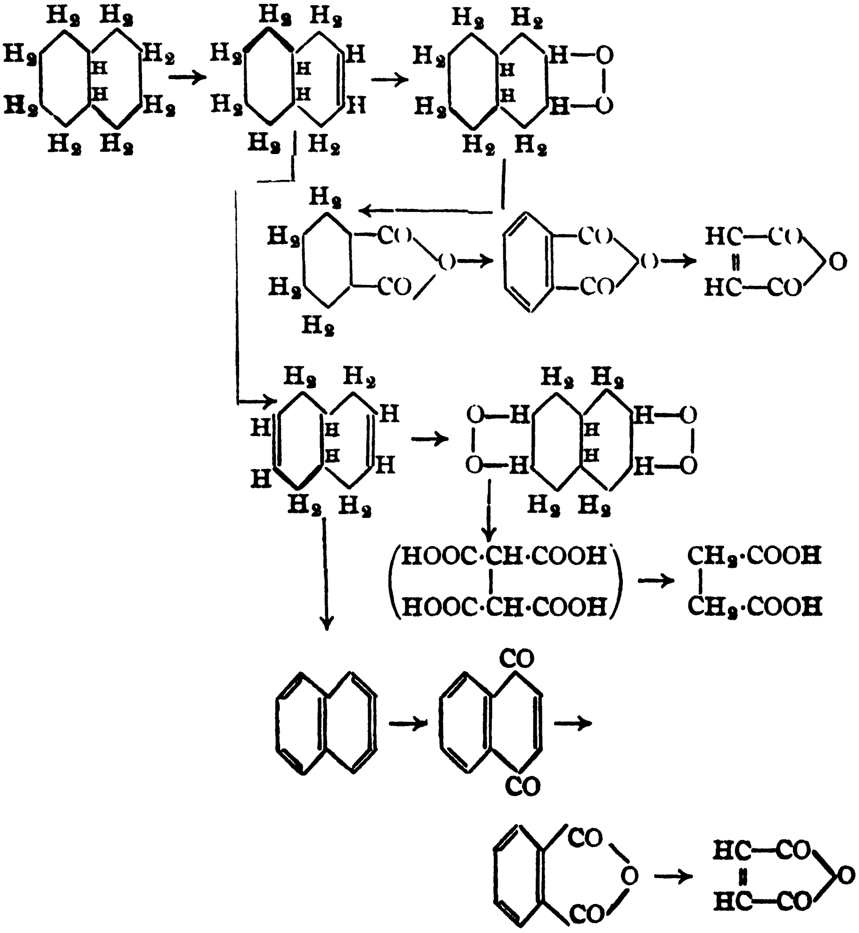
Thus it will be seen that under approximately the same conditions but with varying temperatures, the maximum yield of phthalic acid obtained from naphthalene, phenanthrene and decalin are 60·01%, 22·35% and 37·48% respectively, the yield being intermediate in the case of decalin. This is to be expected not only from the molecular structure of the three hydrocarbons in relation to phthalic acid but also from their heat of reaction which along with the high temperature necessary in case of phenanthrene makes the control of the process very difficult.

Mechanism of Oxidation.—The oxidation of these hydrocarbons appears to follow a somewhat different course from the oxidation of aromatic hydrocarbons. The intermediate products obtained from *cyclo*hexane are unsaturates, peroxides, acraldehyde, pyruvic acid, acetaldehyde and acetic acid while any cyclic alcohol or ketone or formaldehyde could not be identified. This may be represented by the following scheme :—



As benzene and its usual oxidation products could not be found, it is assumed that the oxidation does not appreciably proceed through benzene and maleic acid.

In the case of decalin, the following products were identified :—phthalic acid, maleic acid, succinic acid, benzoic acid (traces), 1 :4-naphthaquinone and formaldehyde. Their formation may be explained by the following scheme :—



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VARIATION OF THE ABSOLUTE RATES OF MIGRATION AND TRANSPORT NUMBER OF ELECTROLYTIC IONS WITH DILUTION.

By N. C. Sen-Gupta and S. K. Mitra.

Onsager (*Physik. Z.*, 1926, **27**, 388 ; *Trans. Faraday Soc.*, 1927, **23**, 341) has deduced equations for the equivalent conductivity and ionic mobility in dilute solutions of strong electrolytes. The equations are free from arbitrary constants and the conductivities can be easily evaluated with the help of them. A limiting equation for the transport number can also be deduced from the equations of Onsager (*loc. cit.*). The conductivity equation has been found by Shedlovsky (*J. Amer. Chem. Soc.*, 1932, **54**, 1411) to be valid for uni-univalent electrolytes upto a concentration of about 0·0001N. The researches of McInnes and co-workers (*Chem. Rev.*, 1932, **11**, 171) have also shown that the transport number equation holds for uni-univalent electrolytes in dilute solutions.

The absolute velocities and transport numbers of the anions of aqueous solutions of KCl, KNO_3, and K_2SO_4 have been measured at concentrations ranging between 0·04N and 0·001N by the method of moving boundaries using Mukherjee's cataphoretic tube. The results have been discussed in the light of the limiting equations of Onsager (*loc. cit.*).

THEORETICAL.

If l_c represents the mobility of an ion at a concentration C, and l_o, the same at infinite dilution then according to Onsager (*loc. cit.*)

$$l_c = l_o - \left[\frac{0{\cdot}9838 \times 10^6}{(DT)^{3/2}} \, w l_o + \frac{28{\cdot}95\, Z_i}{(DT)^{1/2}.\eta}\right]\sqrt{(Z_1 + Z_2)C} \qquad (i)$$

where D is the dielectric constant of the solvent, T, the temperature; Z_i is the charge carried by the particular ion; η is the viscosity of the solvent ; C is the equivalent concentration ; Z_1 and Z_2 are the respective valencies of the anions and the cations:

$$w = Z_1 Z_2 \frac{2q}{1+\sqrt{q}} \text{ ; and } q = \frac{Z_1 Z_2 (l'_o + l''_o)}{(Z_1 + Z_2)(Z_2 l'_o + Z_1 l''_o)} ;$$

where l'_o and l''_o are the limiting mobilities of the cations and anions.

The equation may be put in a simpler form as

$$l_c = l_0 - (\alpha\, l_0 + \beta)\sqrt{C} \qquad \ldots \quad (ii)$$

For uni-univalent electrolytes at 35° the equation reduces to

$$l_c = l_0 - (0{\cdot}168\, l_0 + 27{\cdot}1)\sqrt{2C}.$$

For the sulphate ion in the uni-bivalent electrolyte K_2SO_4, the relation is

$$l_c = l_0 - (0{\cdot}307\, l_0 + 54{\cdot}2)\sqrt{3C}.$$

The equation for transport number deduced from the relations of Onsager is of the following form

$$\left(\frac{\partial T_+}{\partial \sqrt{C}}\right)_{C \to 0} = \frac{\beta}{\Lambda_0}\left[T_+(Z_1+Z_2)-Z_1\right]\sqrt{Z_1+Z_2} \qquad \ldots \quad (iii)$$

where T_+ represents the cation transference number, Λ_0, the equivalent conductivity of the electrolyte at infinite dilution and β is the constant of Onsager's equation equals to 27·1 for dilute aqueous solutions at 35°.

EXPERIMENTAL.

Recrystallised potassium iodoeosinate at suitable concentrations has been used as the indicator solution. All the solutions have been prepared by direct weighing with pure conductivity water having specific conductivities lying between $1{\cdot}2 \times 10^{-6}$ and $1{\cdot}3 \times 10^{-6}$ mho (For detailed description of the procedure compare Sen-Gupta (*This issue*, p. 685).

Solvent Correction That the transport number measurements in dilute solutions must be corrected for the conduction of the solvent impurities was first pointed out by Longsworth (*J. Amer. Chem Soc.*, 1932, **54**, 2741). Longsworth derived the following relation between $T_{\text{corrected}}$ and T_{observed}

$$T_{\text{cor}} = T_{\text{obs}}\left(1 + \frac{K_w}{K_s}\right) \qquad \ldots \quad (iv)$$

where K_w represents the conductivity of the water used and K_s that of the solution. The relation is only approximate since the conductivity of the solvent impurities is influenced by the electrolyte dissolved in water. No solvent correction is, however, necessary for the measured absolute velocity of ions.

RESULTS AND DISCUSSION.

TABLE I.

Variation of the velocity and transport number of the chlorine ion in potassium chloride with dilution.

Temperature = 35°.

Salt conc.	T_{cl}.	T_{cl} (cor.) (mean).	$V_{cl} \times 10^5$.	$V_{cl} \times 10^5$ (mean).
0·04N	0·503		83·5 cm./sec.	
	0·504	0·504	83·6	83·5 cm./sec.
	0·504		83·6	
0·02N	0·502		86·4	
	0·504	0·503	86·1	86·3
0·01N	0·503		88·4	
	0·503	0·503	88·3	88·4
	0·503		88·4	
0·005N	0·503		90·0	
	0·504	0·504	90·1	90·1
	0·504		90·1	
0·002N	0·500		91·6	
	0·501	0·503	91·6	91·6
	0·500		91·6	
	0·500		91·6	
	0·500		91·7	
0·001N	0·498		92·4	
	0·500	0·504	92·4	92·4
	0·500		92·2	
	0·499		92·0	
	0·499		92·6	
			92·3	
Limit at infinite dilution	**From graph**	0·503	—	94·3

TABLE II.

Variation of the velocity and transport number of the nitrate ion in potassium nitrate with dilution.

Temperature = 35°.

Salt conc.	T_{NO_3}	T (cor.) (mean).	$V_{NO_3} \times 10^5$.	$V_{NO_3} \times 10^6$ (mean).
0·04*N*	0·481	0·481	75·0 cm./sec.	75·0 cm./sec.
0·02*N*	0.483	0·483	78·6	78·6
0·01*N*	0·484			
	0·485	0·485	81·8	
	0·485		82·0	82·0
			82·1	
0·005*N*	0·487		83·3	
	0·487		83·5	
	0·487	0·488	83·3	83·3
	0·488		83·3	
	0·487		83·3	
	0·488		83·5	
0·001*N*	0·487	0·490	86·7	$86^{7}3$
	0·487		86·3	
Limit at infinite dilution	From graph	0·490		88·6

TABLE III.

Variation of the velocity and transport number of the sulphate ion in potassium sulphate with dilution.

Temperature = 35°.

Salt conc.	T_{SO_4}	T_{SO_4} (cor.) (mean).	$V_{SO_4} \times 10^5$.	$V_{SO_4} \times 10^5$. (mean).
0·04*N*	0·517	0·517	77·5 cm./sec.	77·5 cm./sec.
	0·517		77·5	
0·02*N*	0·515		81·3	
	0·516		81·4	
	0·517	0·516	81·5	81·4

TABLE III (*contd.*).

Slat conc.	T_{SO_4}.	T_{SO_4}. (cor.) (mean).	$V_{SO_4} \times 10^5$.	$V_{SO_4} \times 10^6$. (mean).
0·02*N*	0·516		81·4	
	0·515		81·3	
	0·516		81·4	
0·01*N*	0.511		83·9	
	0·511	0·511	83·7	83·8
	0·510		83·8	
0·005*N*	0·504		86·8	
	0·505		86·8	
	0·504		87·0	
	0·506	0·506	87·0	87 0
	0·505		87·2	
	0·506		87·0	
	0·505		86·8	
	0·506		87·2	
0·002*N*	0·502		91·2	
	0·505		91·3	
	0·504	0·505	91·3	91·3
	0·504		91·2	
	0·504		91·3	
	0·505			
0·001*N*	0·500		93·2	
	0·501		93·0	
	0·500	0·505	93·1	93·1
	0·501		93·2	
	0·501		93·2	
	0·502			
Limit at infinite dilution ...		0·509		97·5

It will be seen that when the velocity l_c/F is plotted against $\sqrt{C}$ a straight plot is obtained up to a dilution of 0·01*N* in the case of the chloride and the nitrate and up to 0·005*N* in the case of the sulphate. The deviation in concentrated solutions is very large in the case of the sulphate. The slopes of the limiting curves can be calculated from the equation of Onsager. The following table contains the calculated and the observed values.

FIG. 1.

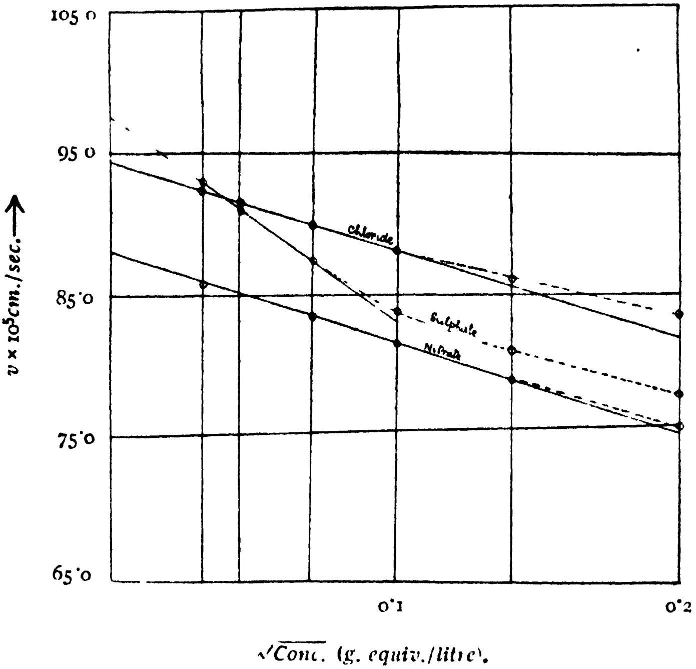


TABLE IV.

Electrolyte	Obs. slope × 10^5	$\frac{\alpha l_0 + \beta}{F} \times 10^5$.
KCl	60	60
KNO_3	72	59·3
K_2SO_4	147	145

Onsager and Fuoss (*J. Phys. Chem.*, 1932, **36**, 2689) suggested an extrapolation of the limiting equation in the following form

$$l_c = l_0 - A\sqrt{C} + B.C \qquad \text{(v)}$$

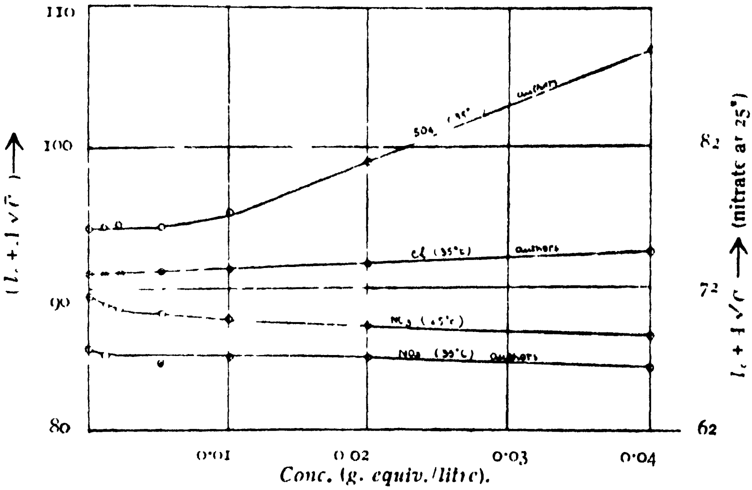
where A equals $\alpha l_0 + \beta$ and B is an arbitrary constant.

$l_c + A\sqrt{C}$ is plotted against C in order to evaluate the constant B.

TABLE V.

Conc. of the K-salt.	$l_c + A\sqrt{C}$			
	Cl (35°).	NO_3 (35°)	SO_4 (35°)	[*]NO_3(25°)
0·04*N*	92·6	84·3	107·6	68·9
0·02	91·7	85·1	98·9	69·4
0·01	91·3	85·1	95·3	69·9
0·005	91·2	84·6	94·3	70·3
0·002	91·1	...	94·5	70·6
0	91·0	85·7	94·3	71·5

FIG. 2.



From an examination of the curves (Fig. 2) it will be seen that the extrapolated equation of Onsager holds good for the case of chloride and sulphate between 0·01*N* and 0·04*N*, while the plot is irregular with the nitrate for which *B* has a negative value showing the peculiar character of the nitrate ion.

In Fig. 3 are plotted the cation transport numbers of KCl, KNO_3 and K_2SO_4 together with the results obtained by McInnes and co-workers (*loc. cit.*) at 25° on KCl, KNO_3 and Na_2SO_4. The dotted curves represent the theoretical lines. It will be seen that the limiting slope is only attained in the case of the nitrate and the sulphate at the highest dilution observed.[†]

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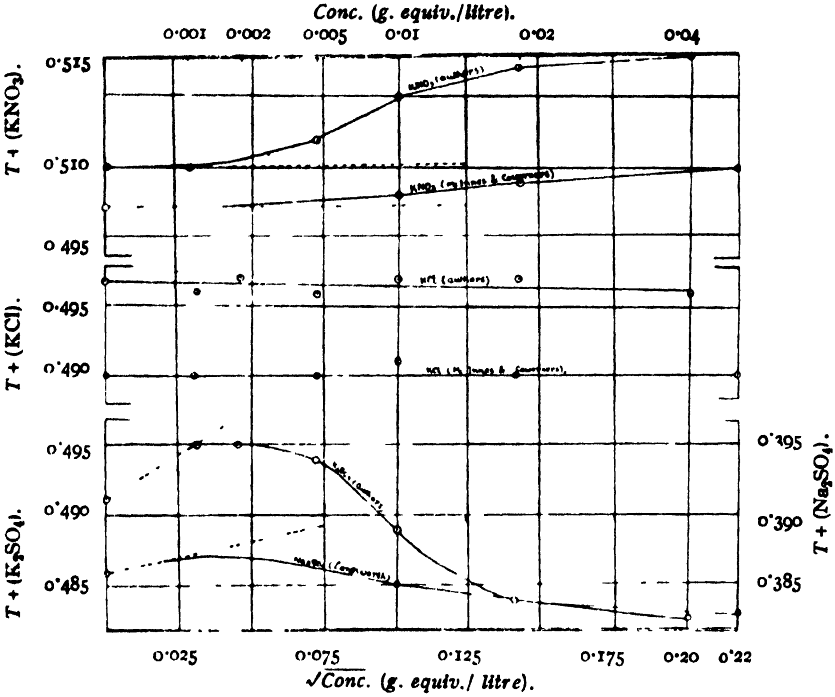
[*] Taken from the transport number data of Longsworth (*J. Amer. Chem. Soc.*, 1935, **57**, 1185) and the conductivity data of Shedlovsky (*loc cit.*)

[†] Hartley and Donaldson (*Trans. Faraday Soc.*, 1937, **33**, 457) have recently measured the transport numbers of certain unsymmetrical electrolytes including K_2SO_4 and observed that the limiting slope is attained in every case at the highest dilution observed by them.

FIG. 3.



SUMMARY.

1. The variation of the transport numbers and absolute rates of migration with dilution has been measured in case of KCl, KNO_3 and K_2SO_4 between dilution 0·04*N* and 0·001*N*. In the most dilute solutions the limiting equations of Onsager have been shown to hold good.

2. Between dilutions 0·005*N* and 0·04*N* the modified equation of Onsager and Fuoss has been shown to hold for the case of the chloride ion and approximately for the sulphate but not for the nitrate.

3. In the case of the nitrate and the sulphate, the transport number curves reach the limiting slope only at the highest dilution (0·001*N*) used by the authors. In the case of chloride the transport number is almost constant within the range of experimental error.

Our best thanks are due to Professor J. N. Mukherjee, D.Sc., for his suggestions and interest in this work. One of us (N.C.S.) also takes this opportunity to thank the University of Calcutta for granting a research scholarship under Professor J. N. Mukherjee during the tenure of which this work has been carried out.

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EXPERIMENTS ON RESOLUTION OF CO-ORDINATED INORGANIC COMPOUNDS INTO OPTICAL ISOMERS. PART II. CO-ORDINATED ZINC COMPOUNDS WITH ACTIVE AND RACEMIC PROPYLENE-DIAMINE.

By Panchanan Neogi and Kanai Lal Mandal.

In this paper complex tripropylenediamine zinc salts have been prepared with three varieties of propylenediamine, *d*, *l* and *r*. Attempts to resolve the racemic compounds have so far not been successful.

Regarding the complex compounds of zinc with *d*-and *l*-propylenediamine, *l*-propylenediamine gave *l*-compounds and *d*-propylenediamine gave *d*-compounds. Similar results have been obtained in the case of complex compounds of cadmium with *d*-and *l*-propylenediamine (Neogi and Mandal, *J. Indian Chem. Soc.*, 1936, **13**, 224).

EXPERIMENTAL.

Zinc tripropylenediamine chloride was obtained by adding 20 g. (70% solution) of propylenediamine in small quantities to a well-cooled solution of anhydrous zinc chloride(10 g.). A white, precipitate which appeared at first, gradually dissolved and a clear solution was obtained. The solution deposited crystals on keeping in a vacuum desiccator for several days. The complex chloride was crystallised from a mixture of equal parts of water and alcohol. It is soluble in water but insoluble in acetone. {Found : N, 23·75 ; Zn, 18·15. $[Znpn_3]Cl_2$ requires N, 23·46 ; Zn, 18·15 per cent}.

Zinc tripropylenediamine bromide was precipitated from a concentrated solution of zinc tripropylenediamine chloride by adding a solution of potassium bromide. It crystallised from a mixture of alcohol and water. The bromide is less soluble in water than the corresponding chloride. {Found: N 18·53 ; Zn, 14·39. $[Znpn_3]Br_2$ requires N, 18·8 ; Zn, 14·54 per cent}.

Zinc tripropylenediamine iodide was obtained as a precipitate by adding a saturated solution of potassium iodide to a concentrated solution of zinc tripropylenediamine chloride. It crystallised from a mixture of water and alcohol. The complex iodide is sparingly soluble in water. It is soluble in acetone. {Found : N, 15·46 ; Zn, 12·4. $[Znpn_3]\ I_2$ requires N, 15·52; Zn, 12·01 per cent}.

Zinc tripropylenediamine thiocyanate, prepared by the action of potassium thiocyanate on the chloride, was crystallised from a mixture of water and alcohol. {Found : N, 28·1 ; Zn, 16·03. $[Znpn_3]\ (CNS)_2$ requires N, 27·8 ; Zn, 16·13 per cent}.

Zinc tripropylenediamine camphor sulphonate was obtained by adding a solution of the silver salt of camphor sulphonic acid to a solution of zinc tripropylenediamine chloride till silver chloride ceased to be precipitated. The mixture was filtered, and fractionally crystallised in a vacuum desiccator. After prolonged drying in a vacuum desiccator, the first fraction was analysed. {Found : N, 11·14 ; Zn, 8·87. $[Znpn_3]\ (C_{10}H_{15}SO_4)_2$ requires N, 11·2 ; Zn, 8·68 per cent}. Other fractions gave similar analytical results. The value of $[\alpha]_D^{30}$ for the first fraction in a 5% solution in 2 dcm. tube was+22·2°. Other fractions yielded similar rotations. The complex salt obtained after removal of the residue was found to be inactive.

Zinc tripropylenediamine bromocamphor sulphonate.—To a solution of zinc tripropylene chloride, a solution of the silver salt of *d*-bromocamphor sulphonic acid was gradually added till it ceased to give a precipitate. The mixture was filtered and the filtrate evaporated in vacuum and fractionally crystallised. After prolonged drying in a vacuum desiccator, the first fraction was analysed.

{Found : N, 9·48 ; Zn, 7·21. $[Znpn_3]\ (C_{10}H_{14}Br\,SO_4)_2$ requires N, 9·26 ; Zn, 7·17 per cent}. Other fractions also gave similar analytical results.

The value of $[\alpha]_D^{30}$ for the first fraction was+47°. Other fractions showed similar rotations. The complex salt after removal of the active residue was inactive.

Zinc Tripropylenediamine Tartrate.—A concentrated solution of zinc tripropylenediamine chloride (5 g.) was triturated with silver tartrate (5 g.) and the extract with hot water evaporated in vacuum and fractionally crystallised. After prolonged drying in a vacuum desiccator the first fraction was analysed and its rotation determined. {Found : N, 19·55 ; Zn, 14·66. $[Znpn_3]\ (C_4H_4O_6)$ requires N, 19·31 ; Zn, 14·94 per cent}. Other fractions also gave similar analytical results. A 5% solution gave $[\alpha]_D^{30} = +27·8°$. Other fractions gave similar rotations. The tartrate when converted into the corresponding chloride was found to be inactive.

Zinc l-*tripropylenediamine chloride* was obtained by combining zinc chloride with *l*-propylenediamine prepared from racemic propylene diamine (*cf.* Baumann, *Ber.*, 1895, **28**, 1179; TSchugaeff, *ibid.*, 1907, **40**, 3461;

1909, **42**, 55). (Found : N, 23·40 , Zn, 18·28. Calc. : N, 23·46 ; Zn, 18·15 per cent). 5% solution in water gave $[\alpha]_D^{30^\circ} = -48·5$, $[M] = -173·6$.

Zinc l-*tripropylenediamine bromide* was prepared as the *r*-variety. (Found : N, 18·96 ; Zn, 14·55. Calc. : N, 18·8 ; Zn, 14·54 per cent). 5% solution gave $[\alpha]_D^{30^\circ} = +45^\circ$, $[M] = -201·1^\circ$.

Zinc l-*tripropylenediamine iodide* was prepared in the same way as the inactive variety. (Found : N, 15·38 ; Zn, 11·78. Calc. : N, 15·52 ; Zn, 12·01 per cent). 5% solution gave $[\alpha]_D^{30^\circ} = -39·2^\circ$, $[M] = -212^\circ$.

Zinc l-*tripropylenediamine thiocynate* was prepared in the same way as the corresponding inactive compound. (Found : N, 27·64 ; Zn, 16·0. Calc. : N, 27·8 ; Zn, 16·13 per cent). 5% solution gave $[\alpha]_D^{30^\circ} = -43·7^\circ$, $[M] = -176·1$.

Zinc d-*tripropylenediamine chloride* was prepared from zinc chloride and *d*-propylenediamine (prepared from *r*-variety, *cf.*, Baumann, *loc. cit.*; Tschugaeff, *loc. cit.*). (Found : N, 23·33 ; Zn, 18·31. Calc. : N, 23·46 ; Zn, 18·15 per cent). 5% solution gave $[\alpha]_D^{30^\circ} = +44·8^\circ$, $[M] = +160·4$.

Zinc d-*tripropylenediamine bromide* was prepared as the corresponding *l*-bromide. (Found : N, 19·11 ; Zn, 14·35. Calc. : N, 18·8 ; Zn, 14·54 per cent). 5% solution gave $[\alpha]_D^{30^\circ} = +44^\circ$, $[M] = +196·7$.

Zinc d-*tripropylenediamine iodide* was prepared as the corresponding *l*-iodide. (Found : N, 15·60; Zn, 12·24. Calc. : N, 15·52 ; Zn, 12·01 per cent). 5% solution gave $[\alpha]_D^{30^\circ} = +38·6$, $[M] = +208^\circ$.

Zinc d-*tripropylenediamine thiocyanate* was prepared as the *l*-thiocyanate. (Found : N, 27·82; Zn, 16·10. Calc. : N, 27·8; Zn, 13·13 per cent). 5% solution gave $[\alpha]_D^{30^\circ} = +41$, $[M] = +165·2$.

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THE REDOX POTENTIAL OF LACTATE-PYRUVATE SYSTEM.

By S. C. Ganguli.

The lactate-pyruvate system is directly involved in the carbohyrate metabolism of living systems. Consequently it has been the subject of study of many authors. Its redox potential has been measured by Barron and Hastings (*J. Biol. Chem.*, 1933, **107**, 567), Banga, Laki, and Szent-Gyorgyi (*Z. physiol. Chem.*, 1933, **217**, 43), Wurmser and Myer-Reich (*J. chim. phys.*, 1933, **30**, 429) and Baumberger, Jurgensen, and Bardwell (*J. Gen. Physiol.*, 1933, **16**, 961). These authors have shown that in presence of suitable enzymes and electromotive activators this system behaves reversibly and a stable electrode potential is obtained at an inert electrode. The electrode reaction is given by the equation :—

$$\text{Pyruvate} + 2\text{H}^{+} + 2e \rightleftharpoons \text{Lactate}$$

and the electrode potential is given by

$$E_p = E - \frac{RT}{2F} ln \frac{(\text{lactate}')}{(\text{pyruvate}')} - \frac{RT}{F} p_H - \frac{RT}{2F} ln \left\{ \frac{K_p}{K_l} \times \frac{K_l + (\text{H}^{+})}{K_p + (\text{H}^{+})} \right\}$$

where K_p and K_l are the dissociation constants of pyruvic acid and lactic acid respectively. K_p is $3{\cdot}2 \times 10^{-3}$ and K_l is $1{\cdot}55 \times 10^{-4}$. '$\bar{E}$' is the Borsook normal potential which is related with Clark normal potential E_0 by the relationship,

$$E_0 = \bar{E} + \frac{RT}{2F} ln \frac{K_p}{K_l}.$$

The value of E_0 found by Banga (*et al*), Wurmser (*et al*) and Barron and Hastings is + 0·288 volts, whereas Baumberger and co-workers have found $E_0 = +\ 0{\cdot}316$ volts.

All the above investigations were complicated by the facts that :—(*a*) some enzymes were introduced in the system whose behaviour towards electrodes is not very clearly known, (*b*) some dyestuffs were introduced. Barron and Hastings in order to account for the discrepancy state that " The discrepancy between the values given by Baumberger, Jurgensen and Bardwell for the normal potential of the system under consideration

(+ 0·316 volts) and the concordant values obtained by Wurmser and Meyer-Reich, Banga, Laki, and Szent-Gyorgyi, and ourselves is probably due to the use of a dye as the electroactive mediator of too positive a potential, compared with the potential of lactate-pyruvate." It was thought by the present author that if the potential of the lactate-pyruvate system could be measured without the introduction of these complicating factors, then a choice could be made between these two values.

The electro-reduction method described by Ghosh, Raychaudhuri, and Ganguli (*J. Indian Chem. Soc.*, 1932, **9**, 43), was considered suitable for the end in view. Pyruvic acid was partially reduced electrolytically in absence of oxygen at a mercury or platinum cathode and the potential of the polarised electrode was measured from time to time against a $N/10$ calomel electrode. After 6-8 hours a limiting potential was obtained which was steady for more than ½ hour. It was found that this limiting potential could be expressed by the usual thermodynamic formula. The value of E_0 obtained was + 0·325 volts at 30°, rather higher than the value obtained by any of the previous authors. Measurements were made both at mercury and platinum electrodes. But whereas the reduction of pyruvate to lactate took place at a Hg-cathode smoothly between p_H 6·47 and p_H 8·38, pyruvic acid could not be reduced to lactic acid at a Pt-cathode above p_H 7·9. At Hg surface also no readings could be taken above p_H 8·38, the electrolytic reduction product not being pure lactic acid above that p_H

The experimental arrangement was similar to that described by Ghosh, Raychaudhuri and Ganguli (*loc. cit.*) with the following modifications:—

(*a*) The pyrogallic acid tower in the nitrogen purification train was omitted.

(*b*) All glass to glass connections were made with impregnated pressure tube coated outside with vacuum grease. This was found to be as satisfactory as ground-glass joints.

(*c*) In place of the siphon tube and the KCl tube, two agar KCl bridges were used.

In order to prevent the oxidation of pyruvic acid in alkaline solution the following procedure was adopted:—A known volume of buffer solution was introduced in the electrolytic vessel, the stopper put in position and the vessel was de-aerated by a stream of nitrogen, and known amount of pyruvic acid was then introduced through the stop-cock. A pyruvic acid solution of the same concentration and p_H was used as the anolyte. The reduction current was then switched on, the current density being 10^{-4} ampere per sq. cm. Platinum cathodes, when used, were 2 cm. sq. The total lactic and pyruvic acid content of the final solution was estimated in a portion of the solution by the iodoform method. This was necessary in order to ensure that the sum of these two acids represented all the pyruvic acid that was originally added. Pyruvic acid was estimated in another portion of the solution by the colorimetric method of Case (*Biochem J.*, 1932 **26**, 753). Lactic acid was obtained by difference.

Kahlbaum's pyruvic acid, freshly distilled in vacuum, was used. The system is more susceptible to traces of oxygen than the cystine-cysteine system. A slow current of nitrogen was kept passing through the vessel throughout the experiment. The equilibrum was always approached from the same side. With proper precautions it was possible to reproduce the results to within ± 5 mv.

TABLE I.

Readings with Hg-*cathode.*

p_H .	Total conc.	Oxd./Red.	E_h .	E_0 .
6·47	0·01332*M*	0·40/·65	−0·064 volts.	+0·330
6·97	,,	0·750/·320	−0·0793	+0·328
7·15	,,	1·560/·430	−0·0865	+0·325
7·25	,,	0·356/1·680	−0·119	+0·335
7·72	0·01256	1·515/·395	−0·120	+0·326
7·89	,,	0·590/·230	−0·136	+0·324
7·89	,,	0·475/1·435	−0·163	+0·324
8·15	,,	0·695/·312	−0·159	+0·319
8·36	0·01332	0·685/·395	−0·159	+0·335
8·38	,,	0·161/·904	−0·199	+0·326
				Mean +0·327

TABLE II.

Readings with the platinum electrodes.

p_H .	Total conc.	Oxd./Red.	E_h .	E_0 .
6·86	0·01256*M*	10·0/1·0	−0·054	+0·327
6·23	0·01332	1·200/·460	−0·038	+0·323

It was not possible to reduce pyruvic acid at a Pt-cathode above p_H 7·0. Below p_H 7·0 the reduction is also never complete, but lower the p_H, the higher is the percentage of reduction.

That the system lactate$\rightleftharpoons$pyruvate should be able to maintain a stable potential at an inert electrode is rather strange. The work of Conant and Cutter (*J. Amer. Chem. Soc.*, 1926, **48**, 1016) has provided that unlike the reduction of double bonded compounds, the reduction of pyruvate to lactate is not the simple addition of two hydrogen atoms to the molecule but involves the change of two electronic charges as well. Probably when a film of oxygen or oxide is present on the metal surface this type of electron change is not able to charge a noble metal electrode. Ghosh and Ganguli (*Biochem. J.*, 1934, **28**, 381) have shown that the sulphydril system becomes reversively active only when the oxygen film is removed. The lactate-pyruvate system may be another type of system which shows no electron activity at all in presence of the film.

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ON THE STUDY OF SOME MONOFLOPHOSPHATES AND THEIR ANALOGY AND ISOMORPHISM WITH SULPHTES*.

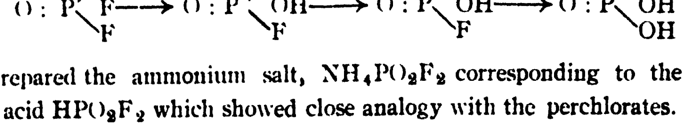
By Harish Chandra Goswami.

The work of Sarkar and Ray (*J. Indian Chem. Soc.*, 1929, **6**, 987) on the homology of the fluo-beryllates and sulphates led to enquire whether other radicals can be found analogous to sulphates. From the table of ionic radii given by Goldschmidt (*Trans. Faraday, Soc.*, 1919, **25**, 282) it follows that compounds of PO_3F ion, if possible to isolate should behave exactly like similar compounds of SO_4 ions (pentavalent positively charged phosphorous ion having the same ionic radius as that of hexavalent positively charged sulpher ion—0·34Å—and the negatively charged fluorine and oxygen ions having approximately equal ionic radii—1·33Å and 1·32Å respectively).

These two ions are isosteric and isoelectric being both bivalent and having thirty two peripheric electrons.

A search in the literature shows that Dorfust and Balz (*Z. anorg. Chem.*, 1927, **157**, 107) have found that all simple and complex salts of fluoborates and perchlorates are perfectly isomorphus. The respective solubilities of these salts are also very close and even the organic salts of these acids are physically and chemically similar. Weinland and Alpha (*Z. anorg. Chem.*, 1899, **21**, 43) prepared potassium, rubidium and caesium monofluophosphates of the formula, $R{\cdot}O{\cdot}P(OH)_3F$, by evaporating a mixture of tertiary phosphates and hydroxides in molecular proportions, dissolved in concentrated hydrofluoric acid. According to Werner they are not to be regarded as true fluo-phosphates (fluorine replacing oxygen), but additive compounds of hydrofluoric acid and ortho-phosphates having the formula $R{\cdot}H_2PO_3HF$, where R represents potassium, rubidium or caesium.

Lange (*Ber.*, 1927, **60**, 965; 1928, **61**, 729) observed that POF_3 hydrolyses, unlike $POCl_3$, in stages probably according to the scheme,



$$O:P\left\langle\begin{matrix}F\\F\\F\end{matrix}\right.\xrightarrow{H_2O}O:P\left\langle\begin{matrix}F\\OH\\F\end{matrix}\right.\xrightarrow{H_2O}O:P\left\langle\begin{matrix}OH\\OH\\F\end{matrix}\right.\xrightarrow{H_2O}O:P\left\langle\begin{matrix}OH\\OH\\OH\end{matrix}\right.$$

and prepared the ammonium salt, $NH_4PO_2F_2$ corresponding to the first stage acid HPO_2F_2 which showed close analogy with the perchlorates.

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* The present work was undertaken in the early part of 1929 and was submitted as a thesis for the M. Sc. Examination in 1930.

The starting material potassium difluophosphate was prepared according to Lange's method (*loc. cit.*). It was then hydrolysed with dilute KOH on the water-bath in the proportion of one molecule of potassium salt to two molecules of the alkali. In order to isolate the expected second hydrolytic product K_2PO_3F, the solution was evaporated in vacuum over sulphuric acid till the salts began to crystallise out. A suspended crystal of potassium sulphate was found to grow uniformly in the filtered solution suggesting that an isomorphous fluophosphate ion has been formed in the solution. The isolation of the fluophosphate by this method is rather tedious and takes a very long time. A second method of isolation of the monofluophosphate was tried directly from phosphoric anhydride and hydrofluoric acid (40 %). The two acids were mixed and neutralised with caustic soda in the cold and the excess of phosphoric acid was then removed by addition of silver nitrate. The monofluophosphate was precipitated by excess of silver nitrate but the yield was very small.

During the progress of the present work there appeared a paper from Lange (*Ber.*, 1929, **62**, 763) in which he described a method for the isolation of ammonium monofluophosphate from ammonium fluoride and phosphorous pentoxide. The other two methods (already tried by us independently) were also anticipated by Lange (*Ber.*, 1929, **62B**, 1084 ; 1931, **64B**, 2772) who made a detailed study of equilibrium between phosphoric acid and water. However, in course of the present work, Lange's method of preparing ammonium fluophosphate was taken advantage of, the molecular volume of K_2PO_3F being very close to that of K_2SO_4, the isomorphism of the sulphate and fluophosphate ions was taken as the criterion of chemical analogy and we prepared copper monofluophosphate analogous to $CuSO_4$, $5H_2O$, that of nickel to $NiSO_4$, $7H_2O$, of cobalt to $CoSO_4$, $6H_2O$, etc. Besides the double salts of ammonium monofluophosphate and the monofluophosphates of the bivalent metals, viz., Ni, Co etc., have been isolated in monoclinic crystals, parfectly isomorphous with the corresponding double sulphates of Locke (*Amer. J. Sci.*, 1902, **27**, 455). The double salts of aluminium monofluophosphate and ammonium monofluophosphate have been prepared and found perfectly isomorphous with the corresponding alum. Mixed crystals of the type, $NiSO_4(NH_4)_2PO_3F$, $6H_2O$ and $RSO_4(NH_4)_2PO_3F$, $6H_2O$ where R represents Co, Cu, Zn, Mn, etc., have also been prepared.

It has been further found that the double salt of ammonium fluoberyllate and nickel fluoberyleate forms mixed crystals and grows uniformly in a saturated solution of the corresponding double salt of the monofluophosphates.

EXPERIMENTAL.

Nickel Monofluophosphate.—Pure nickel chloride was dissolved in the least quantity of water and cooled in ice. An equimolecular quantity of silver monofluophosphate prepared according to Lange (*loc. cit.*) was made into a thin cream with water and run slowly into the nickel chloride solution with constant stirring. Double decomposition took place with the seperation of silver chloride which was filtered and the filtrate was tested for Ag and Cl ions, the excess of one or the other ion being removed by careful addition of a very dilute solution of either nickel chloride or silver monofluophosphate, as the case might be. It was filtered and allowed to crystallise in vacuum over sulphuric acid. The crystals appeared in 2-3 days. (Found : Ni, 20·82 ; P, 10·98 ; H_2O, 44·60. $NiPO_3F, 7H_2O$ requires Ni, 20·73 ; P, 11·0 ; H_2O, 44·60 per cent).

Cobalt monofluophosphate was prepared exactly in the same way as the previous nickel salt. (Found : Co, 22·24; P, 11·09; H_2O, 40·48. $CoPO_3F, 6H_2O$ requires Co, 22·23 ; P, 11·69 ; H_2O, 40·76 per cent).

Copper monofluophosphate was prepared in a similar way to that of nickel. The copper salt is very difficult to crystallise. At first basic copper fluoride separates out which is removed from time to time by filtration and finally a few crystalls are obtained.

It was more conveniently prepared in a fine condition by the addition of alcohol to the ice-cold solution of copper monofluophosphate. (Found : Cu, 25·09 ; P, 12·34 ; H_2O, 35·80. $CuPO_3F, 5H_2O$ requires Cu, 25·25 ; P, 12·35 ; H_2O, 35·85 per cent).

Zinc monofluophosphate was prepared in solution in a similar way to that of the nickel salt, and was crystallised with equal difficulty. The caystallisation was only effected by cautiously adding absolute alcohol to the zinc monofluophosphate solution which was cooled in ice. The solution was stirred all along and fine crystals were obtained which was filtered and dried in vacuum. Kuhn (*Schweigger's J.*, 1830, **60**, 337) and Hannay (*J. Chem. Soc.*, 1877, **32**, 382) prepared an analogous pentahydrated zinc sulphate. (Found : Zn, 25·65 ; P, 12·24 ; H_2O, 35·39. $ZnPO_3F, 5H_2O$ requires Zn, 25·69 ; P, 12·26 ; H_2O, 35·57 per cent).

Other hydrate of the zinc compound could not be obtained.

Preparation of the Double Salt of Nickel and Ammonium Monofluophosphate.

Nickel monofluophosphate and ammonium monofluophosphate were taken in equimolecular proportion and dissolved in the least quantity of water and allowed to crystallise under low vacuum over fused calcium chloride.

The crystals were obtained in a few days and were dried under folds of blotting paper and analysed. In the mother liquor crystals of nickel ammonium sulphate grows uniformly. [Found : Ni, 14·54 ; P, 15·25 ; F, 9·0. $NiPO_3F\ (NH_4)_2\ PO_3F, 6H_2O$ requires Ni, 14·57 ; P, 15·55 ; F, 9·55 per cent].

The hexahydrated crystals are unstable at the ordinary temperature. It loses four out of its six molecules of water of crystallisation and falls into a fine powder. The dehydrated salt is very stable and retains the two molecules of water of crystallisation even at 100°.

Cobalt Ammonium Monofluophosphate.—Equimolecular quantities of cobalt monofluophosphate and ammonium monofluophosphate were dissolved in the least quantity of water and crystallised. [Found : Co, 14·80 ; P, 15·52. $CoPO_3F(NH_4)_2PO_3F, 6H_2O$ requires Co, 14·79 ; P, 15·53 per cent).

The hexahydrated crystals are unstable and loses four molecules of water of crystallisation. The double salt of ammonium monofluophosphate and copper, manganese, zinc, and magnesium fluophosphate could not be obtained.

Preparation of the Alum.

Aluminium Ammonium Monofluophosphate.—An equivalent quantity of silver monofluophosphate was added with stirring to an ice-cooled solution of a weighed quantity of aluminium chloride. The solution was filtered and to the filtrate an equimolecular quantity of ammonium monofluophosphate was added. and it was allowed to crystallise under low vacuum over sulphuric acid. The solution turned turbid with the separation of AlF_3 which was filtered off. This was continued for a few days, after which the hydrolysis stopped. Before the solution turned syrupy it was placed in open air. The crystallisation takes a long time. [Found : Al, 5·90; P, 13·49. $Al_2(PO_3F)_3(Am)_2PO_3F, 24H_2O$ requires, Al, 5·91; P, 13·57 per cent].

The Double Salt of Nickel Sulphate and Ammonium Monofluophosphate.—Heptahydrated nickel sulphate and recrystallised ammonium monofluophosphate were taken in the molecular proportion (1 : 1) and dissolved in the least quantity of water and allowed to crystallise under low vacuum over calcium chloride. In a day or two crystals began to appear which were removed and the mother liquor was placed in a glass chamber.

A large number of crystals were obtained which was analysed and the following results were obtained. The percentage of SO_4 was higher and that of P was proportionately lower than the percentage required by the true double salt.

	Ni.	P.	SO_4.
Percentage	14·82	4·123	37·97
Atomic ratio	0·2525	0·133	0·395

Ratio of the metal : ratio of the acid = 1:2·09. Hence the formula of the compound may be written as $(NH_4)_2Ni(PO_3F,SO_4)_2$, 6 H_2O.

From the mother liquor a second set of crystals was obtained in another two days and on analysis it was found to contain 32·74% SO_4. The percentage of SO_4 in the second set of crystals was lower than the first set. It was then thought that it would be possible to isolate the true double salt having the formula $NiSO_4$ $(NH_4)_2$ PO_3F, $6H_2O$ by successive fractional crystallisation.

In the third set of crystal the percentage of SO_4 was still lower and the fourth set of crystal was found to contain 24·04% of SO_4 which in accordance with the formula $NiSO_4$ $(NH_4)_2$ PO_3F, $6H_2O$ requires 24·24% of SO_4.

At this stage the mother liquor was analysed and the ratio of the nickel sulphate and ammonium monofluophosphate was found to be as 1 : 3. It is thus found that the double salt is only stable with excess of PO_3F *ions.*

Preparation of the Mixed Crystals of Cobalt Sulphate and Ammonium Monofluophosphate.—Pure cobalt sulphate and recrystallised ammonium monofluophosphate were weighed out in the molecular proportion (1 : 1) and dissolved in the least quantity of water and allowed to crystallise under low-vacuum over a few lumps of calcium chloride Crystals were obtained in the form of crusts.

	Percentage	Atomic ratio
Co	14·79	0·2506
SO_4	26·47	0·2756
P	6·825	0·2202

Ratio of the metal : ratio of the acid = 0·2506 : 0·4956 = 1 : 1·98
Hence the formula may be written as Co $(NH_4)_2$ $(SO_4, PO_3F)_2$, $6H_2O$.

Preparation of the Mixed Crystal of Copper Sulphate and Ammonium Monofluophosphate.—Pure copper sulphate and ammonium monofluophosphate were mixed in the molecule proportion (1 : 1), dissolved in the least quantity of water and allowed to crystallise in a vacuum desiccator. In a few hours the solution became turbid owing to the separation of copper fluoride. The solution became turbid again and again and each time it was filtered in a new beaker. In two to three days, hydrolysis stopped and at this stage a crystal of the double salt of nickelammonium sulphate was introduced into the liquid. The nucleus was found to grow uniformly. In the mean time a set of crystals was obtained which were washed, dried and analysed.

	Percentage.	Atomic ratio.
Cu	15·36	0·2439
P	6·873	0·2217
SO_4	26·77	0·2788

Ratio of the metal : ratio of the acid = 2439 : 5005 = 1 : 2·052.

Hence the formula may be written as $Cu(NH_4)_2\ (SO_4,\ PO_3F)_2,\ 6H_2O$.

The Mixed Crystal of Zinc Sulphate and Ammonium Monofluophosphate.—Pure zinc sulphate and ammonium monofluophosphate in the proportion of 1 : 1 molecule were dissolved in the least quantity of water and allowed to crystallise in a vacuum desiccator. Just like copper the solution went on hydrolysing which did not stop for a long time. When the hydrolysis ceased, it gradually turned into a jelly and did not crystallise at all. The crystals were only obtained by the introduction of nuclei of the double salt of nickelammonium sulphate. The nuclei grew uniformly in the liquid. The nuclei were then taken out and the zinc salt thus obtained was broken up to remove the nuclei and then analysed.

	Zn	SO_4	P.
Percentage	15·07	26·38	6·703
Atomic ratio	0·2458	0·2748	0·2162

Ratio of the metal : ratio of the acid = 2458 : 4910 = 1 : 1·997.

Hence its formula may be written as $Zn\ (NH_4)_2\ (SO_4,\ PO_3F)_2,\ 6H_2O$.

The Mixed Crystals of Manganese Sulphate and Ammonium Monofluophosphate.—The salt was prepared by a similar method to that of the zinc salt.

	Mn.	SO_4.	P.
Percentage	14·25	27·01	6·896
Atomic ratio	0·2594	0·3157	0·2224

Ratio of the metal : ratio of the acid = 2594 : 5381 = 1 : 2·074.

The formula of the compound should, therefore, be written as $Mn(NH_4)_2 (SO_4, PO_3F)_2, 6H_2O$.

Method of Analysis.

Estimation of Copper, Nickel and Cobalt.—Copper, nickel and cobalt were estimated electrolytically after decomposing the compound with concentrated sulphuric acid.

Estimation of Aluminium, Zinc and Manganese.—Aluminium was estimated as phosphate, and zinc and manganese as pyrophosphate after the removal of hydrofluoric acid with concentrated sulphuric acid.

Estimation of Phosphorus.—The compound was first decomposed with nitric and hydrochloric acids on the water-bath ; it was evaporated to dryness two to three times after which it was extracted with water and phosphorus was percipitated as ammonium phosphomolybdate. It was then dissolved in ammonia, phosphorus pereciptated with magnesia mixture and ignited and weighed as $Mg_2P_2O_7$.

Estimation of Sulphates.—The compound was decomposed with concentrated nitric acid. Nitric acid was then removed by evaporation with concentrated hydrocholoric acid for several times on the water-bath. It was then extracted with water and precipitated with barium chloride solution and weighed as $BaSO_4$.

Estimation of Fluorine.—The compound was fused with sodium carbonate, extracted with water and neutralised with nitric acid. It was then made slightly alkaline with caustic soda and silver nitrate was added to it. Ag_3PO_4 formed was removed by filtration and sodium chloride was added to remove the excess of silver ion. The solution was filtered and fluorine was estimated according to the method of Stark and Thorin (*Z. anal. Chem.*, 1912, **51**, 14).

Estimation of water of crystallisation.—Water of crystallisation was determined according to Jannasch and Penfield's method. In simple salts the weight of water gave the water of crystallisation, whereas in case of double salts with ammonium salt, the total water obtained minus the weight of water corresponding to the hydrogen of ammonium gave the actual weight of water of crystallisation.

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AN X-RAY INVESTIGATION OF THE CRYSTALS OF *p*-AMINOBENZOIC ACID. THE SPACE GROUP.

By Mata Prasad, M. R. Kapadia and V. C. Thakar.

Crystals of *p*-aminobenzoic acid [$C_6H_4(NH_2)(COOH)$] belong to the monoclinic prismatic class. It is difficult to obtain them in a well developed form. For the purpose of the present investigation the crystals were prepared by the slow evaporation of the solution of the substance in rectified spirit. The crystals which were obtained by repeated crystallisations were in the form of rhombic plates. The shorter diagonal of the plates was found to be the *b*-axis by means of Laue photograph, taken with the flat face normal to the beam. Only three faces, *viz.*, (100), (101) and $(10\bar{1})$ which contain the *b*-axis are mentioned by Groth ("Chemische crystallographie," **IV**, p. 509). By taking several rotation photographs, it was found that the flat face is (101). The crystal was then suitably adjusted and the rotation photographs were taken about *a*, *b* and *c* axes (Plates I, II and III) and about $10\bar{1}$ and 101 axes. The last two photographs were taken for the sake of confirmation. The following were the lengths obtained.

$$a = 12{\cdot}26\ \text{Å}\ ;\ b = 8{\cdot}61\ \text{Å}\ ;\ c = 6{\cdot}30\ \text{Å}.$$

These lengths give the following axial ratio :—

$$a : b : c = 1{\cdot}424 : 1 : 0{\cdot}7316.$$

This ratio agrees with that given in Groth (*loo. cit.*)

$$a : b : c = 1{\cdot}4403 : 1 : 0{\cdot}7312.$$

Further the measurements from the photographs taken about $10\bar{1}$ and 101 axes give the same value of the angle β (100° 10′ as mentioned in Groth).

Oscillation photographs were taken about three crystallographic axes at intervals of 15° and the indices of the planes corresponding to the spots on the oscillation photographs were worked out by means of Bernal's chart. The intensities of the planes were determined by eye-estimation and the usual symbols have been used. The list of the planes observed is given in Tables I and II.

TABLE I.

Axial planes	Prism planes. (hol)	Prism planes. (okl)	Prism planes. (hko)
002 s	101 v. s	011 v. s	110 m
020 m. s.	103 m s.	012 m. s.	120 v. s.
040 m.	101 v. s.	013 s.	130 m. s.
200 v s.	103 m. s.	021 m. s.	140 w.
400 m s	202 m. s	022 m. s.	210 v. s.
600 w.	301 m. s.	023 w.	220 v. s.
	402 s.	031 v. w.	230 w.
	402 v. w.	032 m. s	240 w
	501 w. m.	041 v. w.	310 m. s.
	501 w. m		320 m. s.
	602 s.		330 m.
			340 w.
			430 w. m.
			510 w m.
			520 w.
			610 m
			620 w

Rotation Holograph

Plate I

a-rotation

Plate II

b-rotation

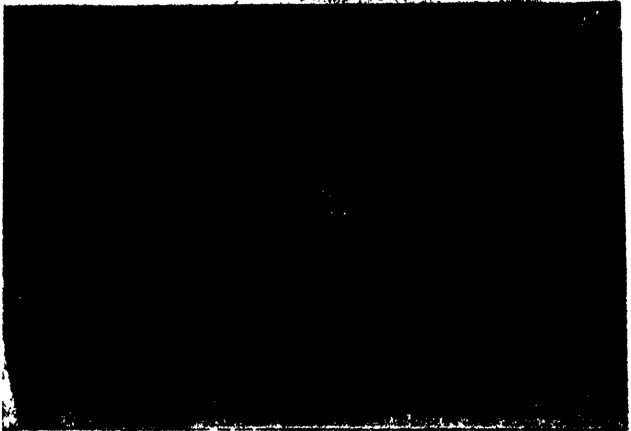

Plate III

c-rotation

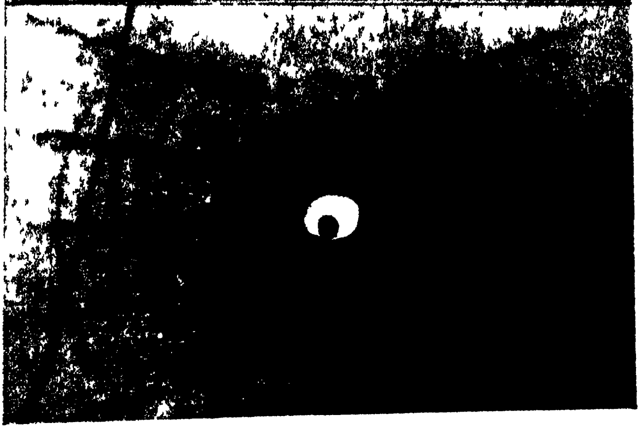

TABLE II.

General planes.

$11\bar{1}$ v.s.	$21\bar{1}$ v.s.	$31\bar{1}$ v.s.	$41\bar{1}$ v.s.	$51\bar{1}$ m.	$61\bar{1}$ w.
$11\bar{2}$ m.s.	$21\bar{2}$ s.	$31\bar{2}$ m. s.	$41\bar{2}$ m.	512 m.s.	611 w.
$11\bar{3}$ s.	$21\bar{3}$ w.	$31\bar{3}$ v.w	$41\bar{3}$ m.	511 m.	$62\bar{1}$ w.
111 s.	211 m.s.	311 v.s.	411 s.	512 w.m.	621 v.w.
112 m.	212 m.s.	312 w.m.	412 m.	521 m.	
113 m.s.	213 w.	$32\bar{2}$ v.w.	421 s.	522 w.	
$12\bar{1}$ v.s.	$22\bar{1}$ v.s.	322 w.	$42\bar{2}$ m.s.	521 m.	
$12\bar{2}$ m.	$22\bar{2}$ m.	$33\bar{1}$ s.	423 v.w.	522 w.m.	
$12\bar{3}$ w.m.	221 s.	$33\bar{2}$ m.	421 m.	$53\bar{1}$ w.m.	
121 m.s.	222 m.s.	331 w.	422 s.		
122 w.	$23\bar{1}$ m.s.	332 w.	431 m.		
123 w.	$23\bar{2}$ m.	$34\bar{1}$ w.m.	431 m.		
$13\bar{1}$ v.s.	231 m.	$34\bar{2}$ m.s.	$44\bar{1}$ s.		
$13\bar{2}$ m s.	232 m.s.	341 v.w.	441 m.s.		
131 m.	241 s.	342 m.			
132 m.s.	$24\bar{2}$ w.				
$14\bar{1}$ v.w.	241 m.				

From the above list of planes it will be seen that (hol) planes are halved if (h + 1) is odd and (oko) halved if k is odd. These halvings correspond to the space group C^5_{2h}. The number of molecules in the unit cell required by the space group is four. The number of molecules calculated from the dimensions of the unit cell, and the density of crystals, 1·393 (Groth), is found to be four (actually 4·01). Hence, it appears that the molecules in the unit cell are asymmetric.

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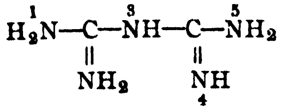
COMPLEX COMPOUNDS OF BIGUANIDE WITH TERVALENT METALS. PART I. CHROMIUM BIGUANIDINES.

By Priyadaranjan Rây and Haribola Saha.

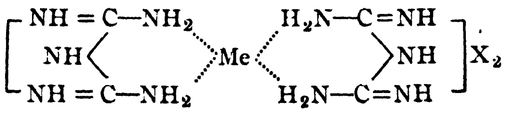
Complex compounds of bivalent metals like Cu, Co and Ni with biguanides, both as free metallic bases and their salts, have long been described (Rathke, *Ber.*, 1879, **12**, 779; Emich, *Monatsh.*, 1883, **4**, 408; Smolka and Friedrich, *ibid.*, 1888, **9**, 227). Besides the simple biguanide, various substituted products of the same, such as the methyl, ethyl and phenyl derivatives, were employed. With each atom of the bivalent metals two molecules of the biguanide base or its salts were found to be associated in the complex formed. The constitution of these interesting complex compounds of strong characteristic colour has not yet been satisfactorily cleared up in spite of repeated investigations on the subject.

The constitution of the biguanide is represented by the formula (I), which is related to those of biuret and guanyl urea. The various constitutions of metallic biguanide complexes, as suggested by different workers (Tschugaef, *Ber.*, 1907, **40**, 1973, formula II ; Ley and Müller, *Ber.*, 1907, **40**, 2950, formula III and IV ; Slotta and Tschesche, *Ber.*, 1929, **62**, 1390, formula IV ; Traube, *Ber.*, 1930, **63**, 2094, formula V), are given below.

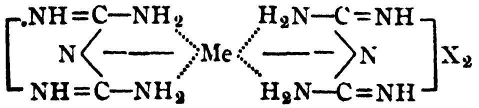


$$H_2\overset{1}{N}-\underset{\underset{NH_2}{\|}}{C}-\overset{3}{N}H-\underset{\underset{\underset{4}{NH}}{\|}}{C}-\overset{5}{N}H_2$$

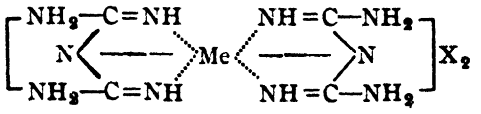
(I)



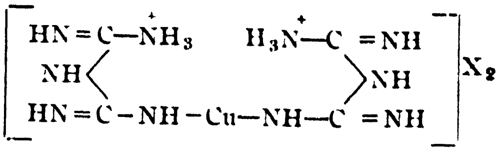
(II)



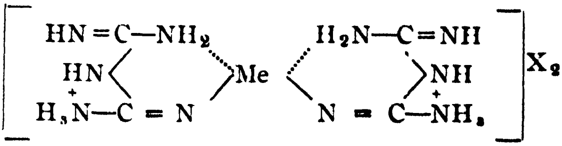
(III)



(IV)



(V).

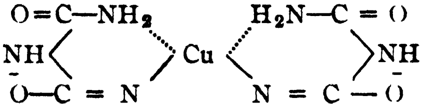


(VI)

[where $X = \overset{-}{\mathrm{OH}}$ or any other equivalent anion, and $\mathrm{Me} = \overset{++}{\mathrm{Cu}}$, $\overset{++}{\mathrm{Co}}$ or $\overset{++}{\mathrm{Ni}}$].

In order to obtain more definite information on the point we have started a systematic investigation on the preparation and properties of a series of biguanide complexes of tervalent metals such as chromium, cobalt, iridium, etc. In the present paper we shall confine ourselves only to the chromium complexes of the simple unsubstituted biguanide.

In these chromium complexes each chromium atom is associated with three biguanide molecules and, as the tervalent chromium can exhibit a maximum co-ordination number of six only, each biguanide molecule behaves as a bidentate group occupying two co-ordination positions in the complex. Further, the free chromium biguanide has been obtained in the anhydrous condition having the composition $\mathrm{Cr(C_2N_5H_6)_3}$, as well as the monohydrate $\mathrm{Cr(C_2N_5H_6)_3, H_2O}$. This hydrate forms beautiful, brilliant red crystals, whereas the colour of the anhydrous base, which behaves like ammonia or amines, is somewhat lighter. In solution, however, the complex behaves as a triacidic base. It gives characteristically coloured solid salts of the type $\mathrm{Cr\ (C_2N_5H_6)_3 \cdot 3HX}$, where X denotes any monovalent anion or its equivalent. The fact that each biguanide molecule occupies two co-ordination positions, disposes of the constitutions (III) and (IV) suggested by Ley and Müller (*loc. cit.*), as well as by Siotta and Tschesche (*loc. cit.*), for the bivalent copper, cobalt and nickel biguanide complexes, in which each biguanide molecule is made to occupy three co-ordination positions, making a bivalent metal atom exhibit a maximum co-ordination number of six. Ley and Müller, as well as Slotta and Tschesche, assume that it is the hydrogen atom of the central imino-group which is displaced by the metal atom, and the latter unites with the nitrogen of the imino-group on both sides forming inner metallic complexes. On the other hand, Ley and Werner (*Ber.*, 1913, **46**, 4040) assign a quite different constitution to the copper biuret complex (VII), though the constitutions of biuret and biguanide are closely analogous.



(VII)

In addition, the metal atom in these complexes (III and IV) forms a member of fused four-membered rings, which, as has been established by Werner and Pfeiffer, can seldom be stable, whereas the stability of biguanide metal complexes exceeds that of most of the well-known inner-metallic salts. Furthermore, formula (IV) leaves four NH_2-groups in the molecule in a free state. Hence the biguanide complexes of the three bivalent metals should behave as tetra-acidic bases, whereas they are actually diacidic. According to formula (III), on the other hand, the complex should behave as a neutral body, unless we assume that the imino-groups exert some basic character.

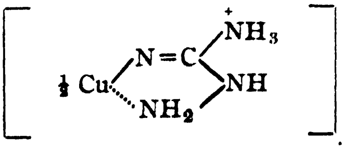
From a study of the increase of acidity by the introduction of metallic atoms into molecules of organic bases or hydroxy compounds, Traube (*loc. cit.*) suggested the constitution (V) for these biguanide metal complexes. The formula does not take note of the co-ordination valencies of copper and hence does not represent the compound as an inner-metallic complex salt which alone can account for its intense colour. Further, the copper atom is shown to replace the hydrogen atoms of one of the end-amino groups of the biguanide base, which is rather unusual and cannot be justified.

Finally, Tschugaeff's formula (II) is also rendered untenable by the fact that it does not represent the complex as an inner-metallic salt, since the central metal atom is linked with the N-atoms of the four amino-groups by co-ordination valencies as in copper tetrammine compounds. The preparation of the anhydrous $Cr(C_2N_5H_6)_3$ by us definitely proves that the primary valencies of the metal atom are satisfied by the removal of one hydrogen atom from each biguanide molecule, and that the basic character of these compounds is due to free amino-groups, and not to the metal atom whose valencies, both normal and co-ordinative, are fully saturated.

From the considerations set forth above it becomes quite clear that the biguanide metal complexes are of the inner-metallic complex salt type; but at the same time they can behave as basic compounds and form salts with acids due to the free amino-groups co-ordinating with H-ions. Each biguanide molecule behaves as a bidentate or chelate group and is linked to the central metal atom both by a primary as well as a secondary valency, like glycine or other amino-acids. Slotta and Tschesche (*loc. cit.*), from the fact that 1:2:3-triphenylbiguanide gives no complex metallic compound, whereas 1:2-diphenylbiguanide and phenylbiguanide give respectively soluble and insoluble metallic complexes, concluded that the hydrogen of the central imino-group is essential for complex formation and is replaced by the metal atom. The argument is not very convincing. Because, the inactivity of the above-mentioned tri-substituted biguanide may be due either to its insolubility in water, or to its enhanced inertness as the result of multiple substitution by phenyl groups. For, we have found that metallic complexes with phenyl (mono) biguanide are less easily formed and are less stable than those with unsubstituted biguanide.

That a hydrogen atom of the imino-group linked to a carbon atom by a double bond can be replaced by a heavy metal atom to give rise to co-ordination compunds of the type discussed here, is best illustrated by the existence of certain complex copper compounds of aminoguanidine of the following composition described by Thiele (*Annalen*, 1892, **270**, 1).

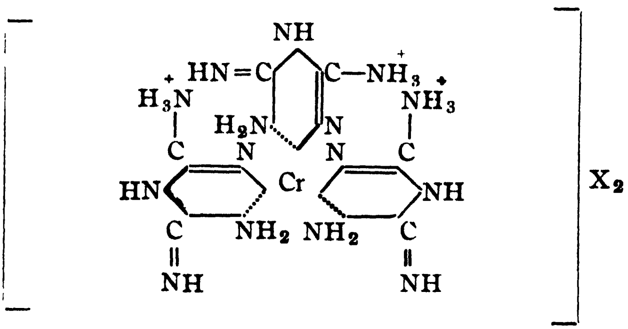
$Cu(CH_5N_4)_2 \cdot 2HNO_3$ and $Cu(CH_5N_4)_2 \cdot H_2SO_4$



(NO_3) (violet crystals).

In these compounds none of the hydrogen atoms of the amino- or the hydrazino-group of the aminoguanidine is likely to be replaced by the metal atom. It is the hydrogen atom of the imino-group that is replaced by the copper atom co-ordinating simultaneously with the end nitrogen of the hydrazino-group to form a five-membered ring.

We, therefore, suggest the formula (VI) for the biguanide complexes of bivalent metals and the formula (VIII) for those with a tervalent metal like chromium. In these, the metal atoms enter into six-membered rings contributing to the stability of the complex, and the number of free amino-groups corresponds to the acidity of the complex base formed. A similar suggestion for the constitution of the biguanide complexes of the bivalent metals has also been offered by Stumpf (Dissertation, Berlin, 1933, p. 24).



(VIII)

These chromium *tris*biguanide salts undergo slow but gradual hydrolysis on warming in dilute solutions, or on keeping, giving rise to a series of hydrolysed products. This is more evident with a solution of the complex hydrate. The mode of hydrolysis may be represented as follows:—

$$\left[\mathrm{Cr(Big\overset{+}{H})_3}\right]\mathrm{X_3 + 2H_2O} \longrightarrow \left[\mathrm{Cr(Big\overset{+}{H})_2{\cdot}OH{\cdot}H_2O}\right]\mathrm{X_2 + BigH_2X}$$

$$+\,\mathrm{2H_2O}\ \Big\downarrow$$

$$\left[\mathrm{(H_2O)_2{\cdot}Cr{\cdot}(OH)_2{\cdot}(Big\overset{+}{H})}\right]\mathrm{X + BigH_2X}$$

$$+\,\mathrm{2H_2O}\ \Big\downarrow$$

[BigH = One molecule of biguanide].

$$\mathrm{[Cr(OH)_3{\cdot}3H_2O] + BigH_2X.}$$

The description of the preparation and properties of these hydrolysed products will form the subject matter of subsequent communications; those of the chromium *tris*biguanide hydroxide and its salts, and a discussion of their constitution have been dealt with in the present paper.

EXPERIMENTAL.

Chromium Trisbiguanide Monohydrate.—A saturated solution of chrome alum was added, drop by drop, with stirring to a cold solution of biguanide sulphate in an excess of strong caustic liquor (30%NaOH). A dark red solution was obtained without any noticeable separation of chromium hydroxide, and bright red prismatic crystals separated readily from the solution in quantities. The solution with the crystals was cooled in ice until no more solid separated and was then filtered on the pump. The crystals were washed with cold water, purified by recrystallisation from hot water in presence of a little caustic soda and dried in air, free from carbon dioxide. {Found : N, 57·16, 57·03; Cr, 13·96, 13.93, 14·06. $[(\mathrm{Big})_2\,\mathrm{Cr}\,(\mathrm{Big}\overset{+}{\mathrm{H}})]\,\mathrm{OH}$ requires N, 56·76; Cr,14·05 per cent}.

The substance is of beautiful crimsom-red colour, which appears ruby-red in large crystals. The crystals are moderately soluble in water, and the solution is strongly alkaline. It liberates ammonia from ammonium salts, precipitates hydroxides of heavy metals from solutions of their salts and behaves as a tri-acidic base in aqueous solution.

$$[(\mathrm{Big})_2\,\mathrm{Cr}\,(\mathrm{Big}\overset{+}{\mathrm{H}})]\,\mathrm{OH}+2\mathrm{H_2O} = [\mathrm{Cr}\,(\mathrm{Big}\overset{+}{\mathrm{H}})_3]\,(\mathrm{OH})_3$$

0·3966 G. of the substance required 3·32 c.c. *N*-HCl for neutralization. $[\mathrm{Cr}\,(\mathrm{Big}\overset{+}{\mathrm{H}})_3]\,(\mathrm{OH})_3$ requires 3·21 c.c. *N*-HCl.

As the solution was strongly coloured and the titration was not carried out potentiometrically but with outside litmus paper indicator, this discrepancy was not unexpected. Measurement of the molecular conductivity and the freezing point of the solution of the base also leads to the same conclusion.

Molecular conductivity at 29°.

v (dilution) ...	32	64	128	256	512	1024
μv ...	132·9	187·2	235·7	292·2	346·2	404·1

The values at higher dilutions are likely to be somewhat vitiated by hydrolysis.

The equivalent conductivity of the base deduced from the above values may be compared with those for ammonia, amines, biguanide and copper biguanide.

Equivalent conductivity for the bases.

$[\mathrm{Cr\,(Big\overset{+}{H})_3}]\,(\mathrm{OH})_3$.

v (dilution)		10·7	21·4	42·8	85·6	171·2	Temp = 29°
λ_v		44·3	62·4	78·6	97·4	115·4	
v	8	16	32	64	128	256	
λ_v NH_3	3.21	4·35	6·52	9·29	13·4	19·0	Temp. = 25°*
λ_v CH_3NH_2	15·1	21·0	28·9	39·3	53·9	70·0	
λ_v $(CH_3)_2NH$	17·2	24·0	33·2	45·3	61·2	80·7	

* Walden, das Leitvermogen der Lösungen—II Teile, pp. 82-83, 1924.

v	300	450	900	
λ_v Biguanide	153·0	153·0	157·5	Temp. = 37°.†
λ_v Cu-*bis*biguanide	74·0	76·5	91·5	

† Deduced from Stumpf's data (*loc. cit.* p. 41)

A comparison of the above values indicates that the chromium *tris*-biguanide hydroxide is a considerably stronger base than ammonia, methylamine, dimethylamine and copper-*bis*biguanide hydroxide, but appears to be somewhat weaker than the free biguanide hydroxide. This comparison is evidently a very rough one due to the differences in temperature of measurements, for which proper allowances should be made.

Definite evidences regarding the tri-acidic nature of the base, are, however, furnished by the preparation of a series of crystalline salts of the base as described hereafter, in which a molecule of the base is found to combine with three equivalents of the acid, as well as by determination of the valeney of the complex ion with the help of Ostwald-Walden's rule from the measurement of equivalent conductivity of its hydrochloride.

A determination of the freezing point of an aqueous solution of the base also supports the above conclusions.

Molecular weight from the freezing-point.

Substance (g/100 c.c.)	Depression. Δ	Mol. wt. m	Vant Hoff's factor $i = M/m$	Degree of dissociation. $\alpha = i-1/n-1$.
0·2496	0·04°	115	370/115 = 3·217	0·75

[where M = mol. wt. calculated; n = number of ions into which the base is dissociated = 4].

The magnetic susceptibility of the substance measured in a Curies balance at 31° gave a value of $\chi_m = 10·47 \times 10^{-6}$, whence $P_{\text{Weiss}} = 10·15$, which is almost identical with those for all complex chromium ammines and salts, as well as for the simple chromium ion—Cr^{+++}.

The substance decomposes on prolonged boiling with mineral acids giving rise to chromic salts. Strong boiling alkali precipitates chromium hydroxide from a solution of the substance with evolution of ammonia

On keeping a cold alkaline solution of the chromium *tris*biguanide hydroxide for some time, the red colour of the solution gradually turns reddish violet and rose-red silky crystals of a hydrolysed product are occasionally deposited from the solution. A similar change occurs with the dilute aqueous solution of the base itself.

Chromium Trisbiguanidine.—The monohydrate $[Cr(Big)_3]H_2O$ did not lose any weight on being kept over concentrated H_2SO_4 in vacuum. When heated, however, to 150-160° for about 40 hours it lost 4·84% of its weight.

Percentage of water in the monohydrate = 4·87. When heated to 200°, the substance commences to decompose. [Found : N, 59·41. $Cr(Big)_3$ requires N, 59·67 per cent].

This anhydro-base is insoluble in all organic solvents. It readily absorbs water to regenerate the monohydrate. The anhydro-base is brick-red in colour.

Chromium Trisbiguanide Hydrochloride.—This was prepared by treating the solid base in a mortar with cold (ice cooling) dilute hydrochloric acid till the mixture became slightly acid. The yellow crystals of the hydrochloride formed were filtered and washed with a little ice-cold water. The crude crystals were then dissolved in the least quantity of hot water, the solution was filtered and cooled in ice. Pure crystals of the hydrochloride separated from the filtrate. The yield of the product could be increased by adding a saturated solution of ammonium chloride to the filtrate. The crystals were filtered, washed at first with ice-cold water and then with absolute alcohol. These were dried in air.

The hydrochloride was also prepared by the action of ammonium chloride upon the base. When the solid base was rubbed in a mortar with a concentrated solution of ammonium chloride, the hydrochloride of the base was formed with evolution of ammonia. {Found : N, 45·2, 45·4; Cl, 23·14, 23·11; Cr, 11·32, 11·35. $[Cr(BigH^+)_3]Cl_3$ requires N, 45·50; Cl, 23·08; Cr, 11·27 per cent}. The substance forms yellow octahedral crystals, soluble in water.

Equivalent conductivity at 30°.

v (dilution)	16	32	64	128	256	512	1024
λ_v	97·05	106·0	115·7	122·6	128·8	134·8	139·3
λ_∞	147·4	145·0	145·6	145·0	145·5	147·2	148·0
Mean λ_∞	146·0						

λ_{32} (after 5 days) = 97·16.

The λ_∞ value is calculated from Walden's formula :—

$\lambda_\infty = \lambda_v(1 + n_1 . n_2 \times 0{\cdot}692 \times v^{-\frac{1}{2}})$, where v=dilution, n_1 and n_2 are the valencies of the ions.

The valency of the complex ion, according to Ostwald-Walden's rule, is given by $\lambda_{1024} - \lambda_{32} = 139{\cdot}3 - 106{\cdot}0 = 33{\cdot}3 = 3{\cdot}33 \times 10$. The valency is, therefore, three.

The equivalent conductivity of the salt can also be compared with those of complex chromium ammine salts having the same valency for the cation, as well as with those of $LaCl_3$.

Temperature = 25°.

v (dilution)	125	250	500	1000
μ_v for $[Cr(CO(NH_2)_2)_6]Cl_3$	296·5	315·4	326·0	340·5

(Werner and Kalkmann, *Annalen*, 1902, **322**, 313).

v	32	64	128	256	512	1024	∞
λ_v for $LaCl_3$	113·1	119·8	126·1	131·9	136·1	140·6	150

(Ley, *Z. physikal. Chem.*, 1899, **30**, 236).

Making allowances for temperature differences, the results are found to compare quite favourably. The values of μ_v for chromium hexaurea chloride can be reduced to those for the corresponding equivalent dilutions. The results further indicate that the mobility of the complex chromium *tris*biguanide ion is nearly of the same order as that of the complex chromium hexaurea cation and considerably lower than that of La^{+++}-ion.

It was found that the equivalent conductivity of the chromium *tris*biguanide hydrochloride decreased on keeping its solution, as the result for

λ_{32} after 5 days' keeping indicates. This is, however, difficult to account for. On the other hand, from the fact that a dilute solution of the salt on keeping undergoes slow hydrolysis, exactly the contrary result might have been expected. This anomaly is possibly connected with a strange property of the solution of the hydrochloride and hydrobromide. From a freshly prepared solution of the hydrochloride all the chlorine is precipitated as AgCl by silver nitrate solution at the room temperature, though the precipitation does not appear to be complete instantaneously and requires shaking for a few moments. But after keeping this solution for 24 hours, addition of silver nitrate produces only a strong turbidity, the addition of a neutral salt like ammonium nitrate, however, immediately precipitates the whole of the chloride as AgCl. This proves that no constitutional change occurs in the aged solution, but the latter develops a power similar to that of protective colloids in preventing the growth of silver chloride particles. This behaviour has been found to be more pronounced in the case of the hydrchloride of the hydrolysed base which will be described in a future communication.

Determination of the molecular weight by freezing-point method supported the conclusion from conductivity measurements.

Subs. (g./100 c.c.)	Depression. Δ	Mol. wt. m	Vant Hoff's factor $i = M/m$	Degree of dissociation $\alpha = i - 1/n - 1$.
0·7198	0·11°	117·8	3·92	0·97

[where M and n have the usual significance].

The result shows that even at 0°, the substance dissociates almost completely into four ions and the whole of the chlorine is in the ionic state.

The yellow solution of the hydrochloride, on keeping for a long time slowly turns violet and deposits rose-red crystals of a hydrolysed product. A similar change of colour at first occurs on boiling the solution, but finally decomposition sets in with separation of chromium hydroxide.

Chromium trisbiguanide hydrobromide was obtained as orange-yellow crystals, moderately soluble in water, by adding a concentrated solution of potassium bromide to a strong solution of the complex hydrochloride. The crystals were filtered, washed and dried over H_2SO_4. {Found : Br, 40·10 ; Cr, 8·83. $[Cr(BigH^+)_3]Br_3$ requires Br, 40·30; Cr, 8·74 per cent}.

Chromium trisbiguanide hydriodide was prepared like the previous compound from the complex hydrochloride and potassium iodide. The substance forms orange-yellow crystals which are much less soluble in water than those of the hydrochloride. The crystals were washed and dried as before. {Found : N, 28·30 ; I, 51·24 ; Cr, 7·12. $[\mathrm{Cr(Big\overset{+}{H})_3}]\,\mathrm{I_3}$ requires N, 28·53 ; I, 51·76 ; Cr, 7·06 per cent}.

Chromium trisbiguanide sulphate was obtained in the form of sparingly soluble, orange-yellow, needle-shaped crystals when a solution of ammonium sulphate was added to that of the complex hydrochloride. The crystals were washed with cold water and dried in air. {Found : N, 40·53 ; Cr, 10·02 ; SO_4, 27·70. $[\mathrm{Cr(BigH)_3}]_2\,(\mathrm{SO_4})_3$, $2H_2O$ requires N, 40·62 ; Cr, 10·06 ; SO_4, 27·85 per cent}. A tetrahydrate is sometimes formed as long (1 cm.) needle-shaped prismatic crystals with orange-red colour.

Chromium trisbiguanide nitrate was prepared by adding a concentrated solution of potassium nitrate to a cold concentrated solution of the complex hydrochloride. The mixture was cooled in ice. The crystals separated were filtered, washed at first with ice-cold water and finally with alcohol. They were afterwards dried over concentrated H_2SO_4. The substance forms orange-yellow crystals, readily soluble in water. {Found : N, 46·50 ; Cr, 9·62. $[\mathrm{Cr(BigH^+)_3}]\,(\mathrm{NO_3})_3$ requires N, 46·60 ; Cr, 9·64 per cent}.

Chromium trisbiguanide nitrite was prepared like the previous compound from the complex hydrochloride and potassium nitrite. It resembles the nitrate in colour and other properties. {Found : N, 50·80 ; Cr, 10·64. $[\mathrm{Cr(BigH^+)_3}]\,(\mathrm{NO_2})_3$ requires N, 51·10 ; Cr, 10·53 per cent}.

Chromium Trisbiguanide Chlorocarbonate.—When a strong solution of sodium carbonate was added to a cold concentrated solution of the complex hydrochloride, the orange-yellow crystals of the chlorocarbonate separated from the solution. The mixture was cooled in ice. The crystals that separated were then filtered, washed and dried as in the case of the chromium *tris*biguanide nitrate. The substance readily dissolves in water giving a solution, strongly alkaline to litmus. {Found : C, 17·24 ; Cl, 15·60; Cr, 11·48, 11·44. $[\mathrm{Cr\ (Big\overset{+}{H})_3}]_2\,\mathrm{CO_3Cl_4}$ requires C, 17·10 ; Cl, 15·57 ; Cr, 11·40 per cent}.

Chromium trisbiguanide carbonate was prepared by adding three molecular proportions of sodium bicarbonate to a cold concentrated solution of chromium *tris*biguanide hydroxide. The mixture was cooled in ice and the normal carbonate was salted out by the addition of a saturated solution of sodium carbonate. The crystals were washed and dried as in the previous case. {Found : C, 19·50 ; Cr, 11·20. $[\mathrm{Cr(BigH^+)_3}]_2\,(\mathrm{CO_3})_3{\cdot}2H_2O$ requires C, 19·40 ; Cr, 11·23 per cent}.

The substance forms orange-yellow crystals, readily soluble in water.

The solution is strongly alkaline to litmus and liberates ammonia from ammonium salts on warming.

Chromium Trisbiguanide Hydrosulphide.—A solution of the chromium *tris*biguanide base was treated with a few drops of ammonia and then saturated in the cold with H_2S. The crystalline precipitate formed was filtered, washed first with ice-water and afterwards with absolute alcohol. The crystals were dried by pressing between filter-papers and keeping overnight in closed air.

The substance forms brownish orange crystals, sparingly soluble in water, and gives out smell of hydrogen sulphide. It reacts alkaline to litmus. {Found : S, 19·90, 20·0 ; Cr, 11·90, 11·20. $[Cr(Big\overset{+}{H})_3]\,(HS)_3$ requires S, 21·10; Cr, 11·45 per cent}.

Comparatively low result for sulphur and high values for chromium indicate slight loss of H_2S.

Chromium trisbiguanide chlorosulphite was obtained as a golden yellow crystalline precipitate by adding a freshly prepared concentrated solution of sodium sulphite to the cold concentrated solution of the complex hydrochloride. The mixture was then cooled in ice and the crystals were washed first with ice-cold water and then with absolute alcohol. They were then dried by pressing between filter-papers and keeping overnight in closed air. The salt is moderately soluble in water. {Found : Cl, 7·10 ; S, 6·55; Cr, 10·6. $[Cr(Big\overset{+}{H})_3]\,ClSO_3,\ H_2O$ requires Cl, 7·27 ; S, 6·55 ; Cr, 10·64 per cent}.

Chromium Trisbiguanide Hydroxosulphite.—When a freshly prepared solution of bisulphite was added, drop by drop, to an ice-cold concentrated solution of the chromium *tris*biguanide hydroxide until the base was partially neutralised, orange-yellow crystals of the hydroxosulphite separated from the solution. These were washed and dried as in the previous case. The crystals are moderately soluble in water and their solution is alkaline to litmus. {Found : S, 6·23 ; Cr, 10·70. $[Cr(BigH)_3]\genfrac{}{}{0pt}{}{SO_3}{OH},\ 2\tfrac{1}{2}H_2O$ requires S, 6·44 ; Cr, 10·46 per cent}.

Chromium trisbiguanide chlorothiosulphate was precipitated in the form of orange coloured silky crystals by adding a solution of sodium thiosulphate to that of the complex hydrochloride. The crystals were washed at first with cold water and then with alcohol. These were afterwards dried in air. The substance is sparingly soluble in water. {Found : Cl, 7·10 ;

S, 12·50 ; Cr, 10·40. $[Cr(Big\overset{+}{H})_3]Cl{\cdot}S_2O_3$ requires Cl, 7·06 ; S, 12·70 ; Cr, 10·35 per cent}

Chromium Trisbiguanide Thiosulphate.—When a solution of the chromium *tris*biguanide hydroxide was mixed with a solution of sodium thiosulphate in the cold and to the mixture a solution of ammonium acetate was added, silky, light orange crystals of the normal thiosulphate were precipitated. These were washed and dried as in the previous case. This normal thiosulphate is very sparingly soluble in water. {Found : S, 18·20 ; Cr, 10·02. $[Cr(Big\overset{+}{H})_3]_2(S_2O_3)_3$ requires S, 18·46 ; Cr, 10·0 per cent}.

Chromium trisbiguanide chlorochromate was obtained as a dark yellow crystalline precipitate when a solution of potassium chromate was added to that of the complex hydrochloride. The crystals were washed with ice-cold water and dried over concentrated H_2SO_4. The substance is sparingly soluble in water. {Found : N, 39·50 ; Cl, 6·80, 6·98 ; Cr (total), 20·0, 19·90 ; Cr (as CrO''_4), 9·90. $[Cr(Big\overset{+}{H})_3]Cl{\cdot}CrO_4, H_2O$ requires N, 40·07 ; Cl, 6·80 ; Cr (total), 19·80 ; Cr (as CrO''_4), 9·90 per cent}.

Chromium Trisbiguanide Chromate.—When a solution of potassium dichromate (1·2 g.) was added to a solution of the complex base (1 g.) in the cold, sparingly soluble yellowish brown crystals of the normal chromate separated out. These were washed and dried as in the case of the previous compound. {[Found : Cr (total), 22·75, 22·50 ; Cr (as CrO''_4), 13·36, 13·10. $[Cr(Big\overset{+}{H})_3]_2(CrO_4)$, $5H_2O$, requires Cr (total), 22·64 ; Cr (as CrO''_4), 13·58 per cent}.

• *Chromium Trisbiguanide Perchromate*.—When 30 % hydrogen peroxide (perhydrol) was added, drop by drop, to an ice-cold solution of the chromium *tris*biguanide hydroxide, dark yellowish brown crystals of the perchromate separated out from the solution. A part of the complex cation was oxidised to perchromate which combined with the rest of the cation to form the very sparingly soluble perchromate of the complex cation. The crystals were washed with ice-cold water and dried over concentrated H_2SO_4. The perchromate decomposes, when acidified, to a blue solution ; the blue colour, however, disappears rapidly with the formation of green chromic salt.The substance gave on analysis :—

Cr (total), 16·94, 17·20 ; N, 35·10 ; O (total), 11·50 (gasometrically), 12·0, on correcting for the chromate left in the solution after the evolution of oxygen. $[Cr(Big\overset{+}{H})_3]CrO_8, 4H_2O$ requires Cr (total), 17·10 ; N, 34·60; O (total), 13·10 per cent.

Low result for oxygen is evidently due to slight decomposition of the perchromate.

Chromium trisbiguanide chlorophosphate was obtained as a sparingly soluble, flesh-coloured crystalline precipitate by adding a solution of disodium hydrogen phosphate to a solution of the complex chloride. The crystals were washed first with cold water and then with alcohol. These were afterwards dried in air. {Found : Cl, 7·20 ; P, 6·36 ; Cr, 10·54. $[Cr(Big\overset{+}{H})_3]\genfrac{}{}{0pt}{}{Cl}{HPO_4}$ requires Cl, 7·30 ; P, 6·38 ; Cr, 10·70 per cent}.

Chromium trisbiguanide camphorsulphonate was obtained as a salmon-coloured crystalline precipitate by neutralising a cold concentrated solution of the complex base with a cold strong solution of camphorsulphonic acid. The crystals were first washed with ice-cold water and then with alcohol. They were afterwards dried over concentrated H_2SO_4. The salt is moderately soluble in water. {Found : S, 9·30 ; Cr, 5·13. $[Cr(Big\overset{+}{H})_3](C_{10}H_{15}OSO_3)_3$ requires S, 9·16 ; Cr, 5·0 per cent}.

From the filtrate of this normal sulphonate a red-violet hydrolysed product was obtained, which will be described in a separate paper.

SUMMARY.

1. Chromium *tris*biguanide hydrate, $[(Big)_2\cdot Cr\cdot(Big\overset{+}{H})]OH$, which behaves as a fairly strong triacidic base in solution, has been prepared in the form of brilliant crimson-red crystals.

2. It has been shown that the complex cation is of the inner-metallic salt type with chromium as the central atom, whose normal valencies are completely saturated by the replacement of one of the hydrogen atoms in each biguanide molecule. The valency of the cation is, therefore, entirely

due to the free amino-groups of the biguanide molecules. This has been definitely proved by the preparation of the anhydrous base, $[Cr(Big)_3]$, chromium *tris*biguanidine. Each biguanide molecule is thus found to behave as a bidentate or chelate group occupying two co-ordination positions in the molecule.

3. A series of salts of the base have been prepared and their properties studied, *viz.*, hydrochloride, hydrobromide, sulphate, nitrate, nitrite, carbonate, chlorocarbonate, hydrosulphide, chlorosulphite, hydroxo-sulphite, thiosulphate, chlorothiosulphate, chlorophosphate, chlorochromate, chromate, perchromate and camphorsulphonate.

4. Indications have been obtained that both the base and the salts undergo slow hydrolysis in dilute aqueous solution giving rise to a series of hydrolysed products.

5. Constitution of the biguanide complexes of bi- and tervalent metals has been fully discussed.

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ON THE MOVING BOUNDARY METHOD FOR THE DETERMINATION OF ABSOLUTE RATES OF MIGRATION AND TRANSPORT NUMBERS OF IONS.

By N. C. Sen-Gupta.

In the present paper the influence of the concentration of indicator ions on the absolute velocity and transport number of chloride, nitrate and sulphate ions has been investigated in centinormal solutions with Mukherjee's cataphoretic apparatus (*Proc. Roy. Soc.*, 1922, **A103**, 102). The concentration adjustments behind a moving boundary have been followed with the same apparatus and thereby the absolute velocity and transport number of the indicator ion estimated with great accuracy. The method as it has been developed in the present paper enables the measurement of the mobility with precision without much trouble and furnishes more information regarding the changes that take place at the boundary than any other single apparatus devised up till now. The method can be used for students' experiments as the equipment can be easily got up.

In the previous measurements (Mukherjee, Mitra and Bhattacharyya, *J. Indian Chem. Soc.*, 1935, **12**, 177; Mukherjee, Mitra and Sen-Gupta, *ibid.*, 1936, **11**, 42) from this laboratory, a **U**-tube with three side-limbs (Fig. 1) a, b and c was taken. The boundary which is of the rising type was initially formed at XX′ between a and b and its upward displacement (x) with time (t) was followed as electrolysis proceeded. The potential gradient in the upper electrolyte AR was measured by observing the potential, v_1, between b and c and then dividing v_1, with the effective length, l, between b and c. The velocity of the leading ion was calculated from the formula,

$$V_A = \frac{x}{t \cdot v_1/l} \qquad \ldots \quad (i)$$

The potential, v_2, between *a* and *b* was also measured against the displacement, x, and the potential gradient in the indicator layer, P_{BR}, was obtained from the relation

$$P_{BP} = v_1/l + dv_2/dx. \qquad \ldots \quad (ii)$$

The absolute rate of migration of the indicator V_B can then be obtained by dividing x/t by the potential gradient in the indicator.

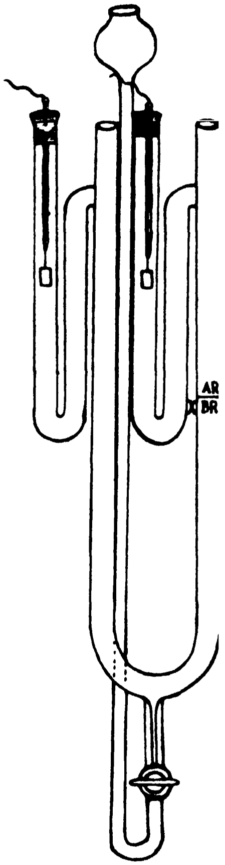


Fig. 1.

When x was plotted against t, a straight line was obtained which tended to become convex towards the x-axis v_2-x and v_2-t curves were not straight but showed a convex curvature towards the v_2-axis, even at the beginning.

In the present arrangement the lowest side-limb was eliminated and the x-t curve was obtained as a straight line. The v_2-x curve was found to be regular on forming the boundary initially at a place well below the side-limbs. The displacement of the boundary with time has been observed in the left limb of the tube which contains no side-limbs ; while the potential measurements across the boundary have been carried out in the limb of the U-tube containing the side-tubes.

Greater care has been taken with regard to the following points than that in previous papers (*loc.' cit*) :

(*a*) All the solutions have been prepared by direct weighing in a 2-litre volumetric flask instead of by the dilution of a stock solution.

(*b*) The potassium iodoeosinate and potassium picrate used as the indicators have been recrystallised from conductivity water.

(*c*) The current has been taken from a battery of accumulator cells giving 110 volts.

(*d*) The current has been read with an ammeter reading directly up to 2×10^{-7} ampere and has been checked with a standard potentiometer.

(*e*) Reversible electrodes have been used.

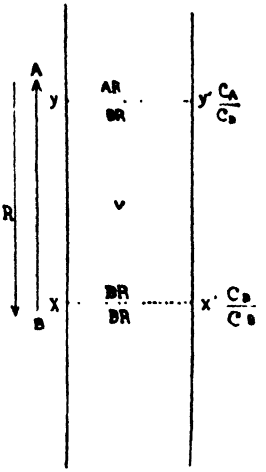
(*f*) The specific conductivities have been measured more accurately with a Hartmann and Braun bridge using a valve oscillator of variable frequency as the source of the alternating current.

Sources of Error.—In the calculation of the transport number by the equation

$$T_A = \frac{v.C_A.F}{i.t} \qquad \ldots \quad (iii)$$

where v represents the volume traced by the boundary; C_A the concentration of the A ion; i, the current strength and t, the time; two types of corrections are necessary as has been indicated by Lewis (*J. Amer. Chem. Soc.*, 1910, **32**, 862) and Longsworth (*ibid.*, 1932, **54**, 2741). However these corrections amount to less than 0·1 in centinormal solutions and need not be discussed for the present case.

Fig 2



Constancy of Current.—In the measurements of McInnes and others (McInnes and Longsworth, *Chem Rev.*, 1932, **11**, 171; Hartley and Moilliet, *Proc. Roy. Soc.*, 1933, **A140**, 141) a given length of the leading solution in the moving boundary tube is continuously displaced by the corresponding length of the less conducting indicator solution. The total resistance of the system therefore goes on increasing and in order to keep the current constant some external arrangement is necessary [*cf.* the elaborate constant current arrangement of McInnes and collaborators (*loc. cit.*) and the thermionic valve arrangement of Hartley and collaborators (Hartley and Donaldson, *Trans. Faraday Soc.*, 1937, **33**, 457)]. With Mukherjee's cataphoretic apparatus, however, since the loss of conductivity in one limb is almost made up by the corresponding gain in the other, the current remains almost constant; hence an adjustment with a hand regulated rheostat serves the purpose.

Potential Gradient in the Leading Solution.

Since the concentration of the leading electrolyte above the boundary does not change with the progress of electrolysis, the potential gradient may in the same way either be directly determined or calculated from formula

$$P_{AR} = \frac{}{K_{AR}.Q} \qquad \ldots \quad (iv)$$

where K_{AR} is the specific conductivity of the liquid AR and Q, the cross-section of the tube. The following table gives some of the results on the potential gradient of the upper liquid determined directly and indirectly from equation (*iv*).

TABLE I.

0·02N-KCl (Temp. 35°). K=0·003312 mho. l=1·267 cm. Q=0·2775 sq. cm.

i (amp) × 10 ^{6}.	v_1(obs).	P_{AR}.	P_{AR} (eq. iv)
925	1·287 volts	1·02 volts/cm.	1·01 volts/cm.
1100	1·515	1·12	1·12
	1·518	,,	,,
1500	2·060	1·63	1·63

It is evident from Table I that the potential gradient in the upper electrolyte may be calculated from the current and cross-section of the tube without direct potentiometric measurements. This procedure was adopted for measuring the potential gradients in the leading solution in the present paper.

Reproducibility of Measurements.

The following table shows the reproducibility of results in a solution of 0·01N-KNO_3 with K_2I of suitable concentration as the indicator solution. It will be evident that the transport numbers do not diminish chronologically as in experiments previously reported (Mukherjee, Mitra and Bhattacharyya, *loc. cit.*; Mukherjee, Mitra and Sen-Gupta, *loc. cit.*).

TABLE II.

0·01N-KNO_3. Temp.=35°. i=200 × 10^{-5} amp. Sp. condty=1632 × 10^{-6}mho.

Time.	Distance moved	T_{NO_3}	V_{NO_3} × 10^5.
340 sec	1·0 cm.	0·480	81·2 cm/sec.
511	1·5	0·479	81·0
681	2·0	0·480	81·2
849	2·5	0·480	81·2
1017	3·0	0·481	81·3

Limits of Adjustment of Concentrations

Tables III—V contain the results on the transport number and absolute velocity measurements of the anions in centinormal potassium chloride, potassium nitrate and potassium sulphate solutions using various concentrations of potassium iodoeosinate as the indicator solution. The results are generally reproducible within about 0·3% when the concentration of the indicator solution is greater than that demanded by equation (v) (*vide infra*), when the indicator solution is more dilute the results are less reproducible. In Fig. 3 are plotted the transport numbers of the leading ions against the concentrations of the indicator, and in Fig. 4, the absolute rates of migration of the leading ions against the specific conductivities of the indicator.

TABLE III.

0·01*N*-KCl (sp. conductivity, 0·001697 mho). Temp. = 35° ± 0·05.

Conc. of the indicator.	T_{Cl} (KCl).	$V_{Cl} \times 10^5$.
0·01073*N*	0·499	87·8 cm./sec
	0·496	87·5
	0·499	87·7
	0·498	87·6
	0·498	87·6
	0·498	87·6
	Mean 0·498 ± 0·0005	**Mean** 87·6 ± 0·15
0·00644*N*	0·503	88·4 cm./sec
	0·504	88·6
	0·501	88·0
	Mean 0·503 ± 0·0015	**Mean** 88·3 ± 0·30
0·00460*N*	0·525	92·3
	0·520	91·5
	Mean 0·523 ± 0·002	**Mean** 91·9 ± 0·40

Conc. of the indicator.	T_{Cl} (KCl).	$V_{Cl} \times 10^5$.
0·00805*N*	0·504	88·6 cm./sec
	0·505	88·8
	0·501	88·1
	0·502	88·2
	Mean 0·503 ± 0·002	**Mean** 88·4 ± 0·35
0·00537*N*	0·501	88·1 cm./sec.
	0·504	88·6
	0·504	88·6
	Mean 0·503 ± 0·0015	**Mean** 88·4 ± 0·25
0·00358*N*	0·537	97·4
	0·547	95·5
	Mean 0·542 ± 0·005	**Mean** 96·4 ± 0·95

TABLE IV.

0·01N-KNO_3 (sp. conducty. = 0·001617 mho). Temp. = 35° ± 0·05.

Conc. of the indicator.	T_{NO_3} (KNO₃).	$V_{NO_3} \times 10^5$.
0·01073N	0·484	81·8 cm./sec.
	0·485	82·0
	0·485	82·1
	Mean 0·485 ± 0·0005	Mean 82·0 ± 0·15

Conc. of the indicator.	T_{NO_3} (KNO₃).	$V_{NO_3} \times 10^5$.	Conc. of the indicator.	T_{NO_3} (KNO)₃.	$V_{NO_3} \times 10^5$.
0·00805 N	0·481	81·3 cm./sec.	0·00644 N	0·480	81·2 cm/sec.
	0·482	81·5		0·481	81·4
	0·483	81·8		0·484	81·9
	0·482	81·5		0·485	82·1
				0·484	81·9
	Mean 0·482 ± 0·001	Mean 81·5 ± 0·25		Mean 0·483 ± 0·002	Mean 81·7 ± 0·4
0·00537 N	0·500	84·5	0·00460 N	0·518	87·0
	0·499	84·5		0·522	87 6
	0·497	84·0			
	0·497	84·0			
	Mean 0·497 ± 0·0015	Mean 84·2 ± 0·25		Mean 0·520 ± 0·002	Mean 87·3 ± 0·3

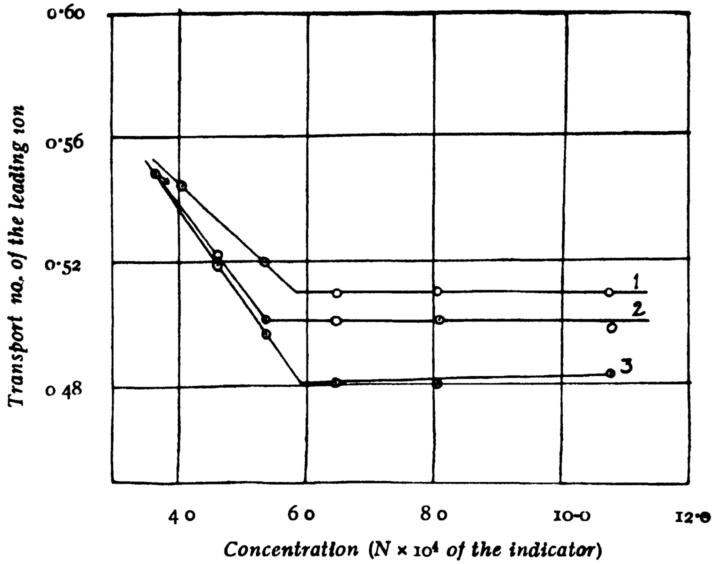
TABLE V.

0·01N-K_2SO_4 (sp. conducty.=0·001582 mho). Temperature=35° ±0·05.

Conc. of the indicator.	T_{SO_4}.	$V_{SO_4} \times 10^5$.	Conc. of the indicator.	T_{SO_4}.	$V_{SO_4} \times 10^5$.
0·01073 N	0·513	84·2 cm./sec.	0·00644 N	0·511	83·9 cm./sec
	0·509	83·5		0·509	83·6
	0·509	83·6		0·510	83·8
	0·513	84·2		0·510	83·8
	0·512	84·1		Mean 0·510±0·001	Mean 83·8±0·15
	0·510	83·6	0·00537 N	0·521	85·6
	Mean 0·511±0·002	Mean 83·9±0·35		0·523	85·8
				0·519	85·3
0·00805 N	0·510	83·6		0·521	85·6
	0·512	83·8		0·521	85·6
	Mean 0·511±0·001	Mean 83·7±0·1		Mean 0·521±0·002	Mean 85·6±0·25
0·00403N	0·541	87·7			
	0·552	89·5			
	0·549	88·9			
	Mean 0·547 ± 0·005	Mean 88·7 ± 0·90			

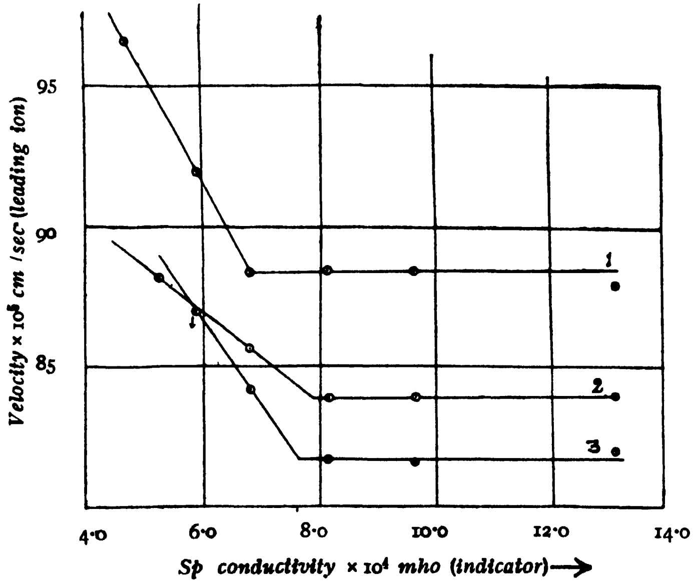
* The above measurements have been carried out in collaboration with Mr. S. K. Mitra.

Fig. 3.



Curves 1-3 refer respectively to sulphate, chloride and nitrate.

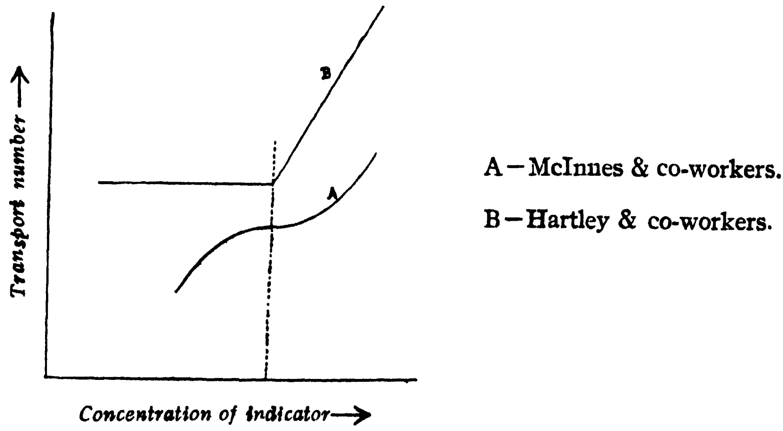
Fig. 4.



DISCUSSION.

The results of various laboratories (*loc. cit.*) show a difference in the nature of adjustment curves. McInnes and co-workers (*loc. cit.*) working with falling boundaries have found that an adjustment is obtained only over a limited range of the indicator concentration on either side of which the results are vitiated. Hartley and co-workers (*loc. cit.*) on the other hand have found that with boundaries of the falling type quite reproducible results are obtained when the indicator solution has any concentration more dilute than that demanded by equation (*v*) (*vide infra*). The shapes of their curves are shown in Fig 5.

Fig 5.



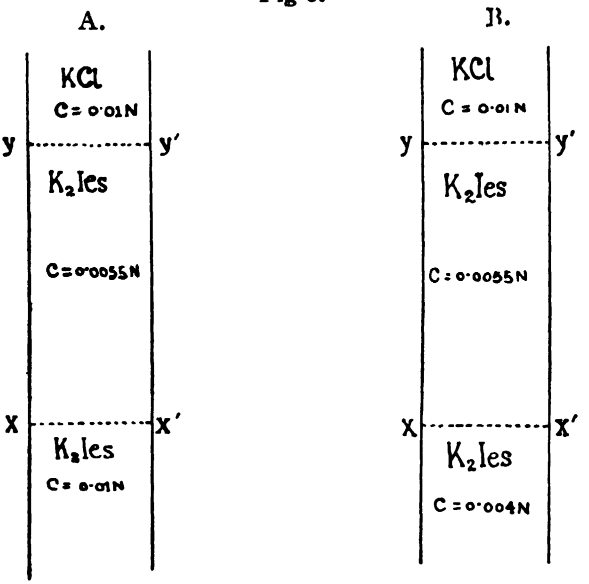
The results of the present measurements, however, show that the range of adjustment is quite unlimited in the higher concentration range of the indicator since similar results have been obtained in the case of all the three electrolytes investigated. Similar observations were also made by Longsworth (*J. Amer. Chem. Soc.*, 1930, **52**, 1897) with rising boundaries between KCl and KIO_3.

The curves may be explained in the following way after the method of Longsworth (*loc. cit.*).

In Fig. 6 A and B are represented the two conditions, where the indicator concentration is respectively more concentrated and more dilute than the adjusted concentration. The following is the density relation between the indicator solutions :

$D_{0·01N} > D_{0·0055N} > D_{0·004}$

Fig 6.



Since in Fig 6A the lighter solution of the indicator is above the concentrated, the arrangement is left undisturbed, while in Fig. 6B the heavier solution of the indicator being above the lighter, the distribution is seriously affected by the difference in density. This will be more clear in the next section where we deal with the measurement of the indicator concentration behind the boundary.

The nature of adjustment curves is exactly similar in the case of the three electrolytes investigated including the weak nitrate ion and the polyvalent sulphate ion. The adjustment depends only on the concentration of the electrolytes and not on their specific electrochemical character.

Another point which may be mentioned is that the transport number increases linearly with C_B , when C_R is less than the adjusted concentration. This linear relationship remains as yet to be explained.

Concentration of the Indicator behind the Moving Boundary.

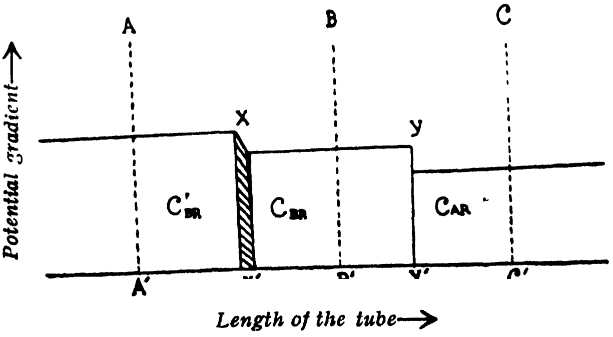
Cady and Longsworth (*J. Amer. Chem. Soc*, 1929, **51**, 1656) observed the increase in the total resistance in an autogenic moving boundary apparatus where a definite volume of the leading solution was displaced by the indicator. They also measured the specific conductivity of the indicator solution behind the boundary with two platinised points. Both measurements showed within about 2% that the concentration of a solution behind a moving boundary adjusted itself according to equation (*iii*). The determination of C_{BR} yields a means of calculating T_B^{BR} and V_B of the indicator ion.

Drew, Collie and Hartley (*Trans. Faraday Soc.*, 1934, **30**, 648) have, however, shown that the method cannot be applied in dilute solutions. They designed an apparatus giving what they called a balanced boundary in which the indicator solution behind the boundary can be continuously transferred to a side vessel and its conductivity determined there. Hacker (*Koll. Chem. Beih.*, 1935, **41**, 147) has shown by external analysis as well as by potentiometric measurements that the relation of Kohlrusch and Weber (*Ann. Physik*, 1897, **62**, 209; *Sitzungsber. Berlin Acad.*, 1897, 936) holds good.

In the previous communication from the laboratory (*loc. cit.*) the potential gradient in the indicator P_{BR} was determined by equation (*ii*), as indicated before and V_B was calculated from the relation $V_B = \frac{x}{t.\ P_{BR}}$. The results however varied as much as 30% and were always higher than the accepted values.

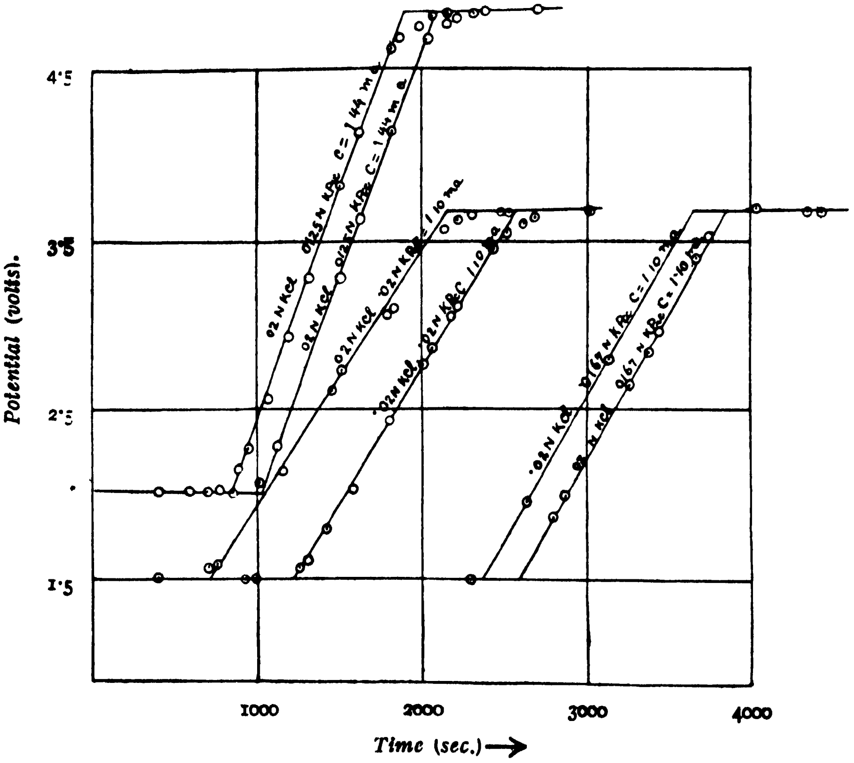
The reason of this will be clear from the following consideration. The indicator BR (*cf.* Fig. 2) cannot be taken exactly at the adjusted concentration initially, it will be a little too concentrated or too dilute. Taking the latter case, the potential gradients along the cataphoretic tube may be represented by Fig. 7. Since C'_{BR} is more dilute than C_{BR} the potential gradient in the former will be greater than that in the latter. The boundary was initially at XX′ and with progress

FIG. 7.



of electrolysis has come to YY′ and a volume of v of the leading solution AR has been displaced by the same volume of the indicator solution BR at the concentration C_{BR}. If the potential V_2 between BB′ and CC′ is measured as the boundary moves then we have, $\frac{dv_2}{dx} = +P_{BR} - P_{AR}$, and adding P_{AR}, to the latter we get P_{BR}. If, however, the potential is measured between AA′ and CC′ as in previous measurements (Mukherjee, Mitra and Bhattacharyya, *loc. cit.*; Mukherjee, Mitra and Sen Gupta, *loc. cit.*) we do not get P_{BR} but any value between P_{BR} and P'_{BR} (potential gradient in C'_{BR} solution). This then is the reason why the P. G. of previous measurements gave so erratic values of the absolute velocities of the indicator ion.

FIG. 8.



In the present investigation a narrow cataphoretic tube with two side-limbs, fused near each other, has been used. The boundary was formed between 0·02*N*-KCl and various concentrations of potassium picrate In Table VI are given the results of a particular set of measurements where the concentration of the indicator was 0·02*N*. Some of the results are also shown in Fig. 8.

TABLE VI.

Conc. of KCl = 0·02*N*. $K_{KCl} = 3312 \times 10^{-6}$ mho. Conc. of K_{Pic} = 0·02*N*. $K_{Pic} = 2271 \times 10^{-6}$ mho Temp. = 35°. Current = 1100×10^{-6} ampere.

Time.	Potential.	Time.	Potential.
0 sec.	1·512 volts	2445 sec.	2·622 volts
300	1·512	2505	2·748
480	1·515	2780	3·072
940	1·515	2820	3·126
1395	1·521	3125	3·558
1700	1·572	3200	3·636
1755	1·596	3270	3·699
2160	2·148	3460	3·695
2195	2·211	3510	3·693

According to the theory of Kohlrausch (*loc. cit.*) and Weber (*loc cit.*) which need not be recapitulated here the concentration of the indicator behind a moving boundary should be adjusted according to the relation,

$$C_A / C_B = T_A / T_B \qquad \dots \quad (v)$$

where C_A and C_B are the concentrations and T_A and T_B are the transport numbers of the leading and indicator ions respectively. It also follows from the relation that

$$V_B / V_A = P_{AR} / P_{BR} \qquad \dots \quad (vi)$$

where V_A is the absolute velocity of the leading ion and V_B that of the indicator ion, P_{AR} and P_{BR} being the two potential gradients.

Substituting the values of P_{AR}, P_{BR} and V_A in equation (*vi*) one gets the value of V_B as the following :—

$$V_{Pic} = \frac{1{\cdot}515}{3{\cdot}693} \times 86{\cdot}3 \times 10^{-5} \text{ cm./sec.} = 35{\cdot}4 \times 10^{-5} \text{ cm./sec.}$$

Since the specific conductivities are inversely proportional to the potential gradients, the specific conductivity of the picrate solution behind the boundary is found to to be

$$\frac{1{\cdot}515}{3{\cdot}693} \times 0{\cdot}003312 = 0{\cdot}001358 \text{ mho.}$$

The corresponding concentration is about 0·01195*N*.

Applying equation (*v*) one gets for $T_{Pic} = \frac{0{\cdot}504 \times 0{\cdot}01195}{0{\cdot}02} = {\cdot}0301.$

Table VIII gives the results of potentiometric measurements with 0·02*N*-KCl as the upper electrolyte and various concentrations of K_{Pic} as the indicator electrolyte.

TABLE VII.

Conc. of KP.	Specific conductivity × 10^6 of the soln. used.	Specific conductivity × 10^6 behind the boundary.	$V_P \times 10^5$ cm./sec.
0·02 *N*	2271	1358	35·4
,,	,,	1357	35·4
0·0167	1889	1359	35·4
,,	,,	1359	35·4
0·0125	1418	1369	35·6

TABLE VIII (*contd.*).

Conc. of KP.	Specific conductivity $\times 10^6$ of the soln. used.	behind the boundary	$V_P \times 10^{\text{[illegible]}}$ cm·/sec.
0·0125*N*	1418	1368	35·6
0·0111	1270	1419	36·9
,,	,,	1416	36·9
0·0105	1228	1523	39·6
,,	,,	1558	40·6

One can easily see from the results that when the indicator solution is more dilute than 0·012*N*, the specific conductivity of the solution behind the boundary is higher than the specific conductivity of the indicator at the adjusted concentration. This rise in the specific conductivity can only take place if some of the leading solution of higher specific conductivity comes inside the indicator layer.

The absolute volocities of the picrate ion obtained in this paper may be compared with that obtained by Ulich (*Trans. Faraday Soc.*, 1927, **28**, 388). He found the mobility of the picrate ion at infinite dilution to be 30·1 at 25° and $l_{\text{Pic}} \times \eta$ to be 0·269, where η is the viscosity of the solvent. Dividing 0·269 with the value of η at 35°, *i.e.*, 0·007208 poise (*Int. Crit. Table*, 1929, **5**, 10) one gets 37·4 as the mobility at infinite dilution at 35°. From this value, the mobility of the picrate ion at a dilution of 0·012*N* at 35° may be calculated by applying Onsager's equation, and is found to be 34·1 and the corrresponding absolute velocity to be $35{\cdot}3 \times 10^{-5}$ cm./sec. The value is in excellent agreement with the value of the velocity of picrate ion found by the author at a concentration 0·012*N* namely $35{\cdot}5 \times 10^{-5}$ cm/sec. Ulich (*loc. cit.*) also gives $l_{\text{Cl}}' / l_{\text{Pic}}' = 2{\cdot}54$ at 25° and 2·20 at 100°. Taking the ratio to be 2·50 at 35° and the absolute velocity of the chlorine ion at 35° to be $83{\cdot}3 \times 10^{-5}$ cm./sec., in 0·01*N* solution, the absolute velocity of the picrate ion is found equal to $35{\cdot}4 \times 10^{-5}$ cm./sec.

SUMMARY.

1. The range of the concentration of the indicator, within which the

transport number and absolute velocity of the leading ion remains constant has been investigated in the case of KCl, KNO_3 and K_2SO_4.

2. It has been found that within the range of experimental accuracy namely about ±0·3% the transport number and absolute velocity remains constant when the indicator liquid is more concentrated than is demanded by the theory of Kohlrausch and Weber. Beyond this range the measured transport number and absolute velocity increases with the diminution in the concentration of the indicator.

3. The concentration adjustments in the indicator solution have been followed potentiometrically and it has been found that with concentrated indicator solutions dilute solutions of constant composition come out in every case. The absolute velocity and transport number of the indicator ion have been calculated from such measurements.

My best thanks are due to Professor J. N. Mukherjee, D.Sc. for suggesting this work and for his advice and to the Calcutta University for granting a research scholarship under Prof. J. N. Mukerjee during the tenure of which this work has been carried out.

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REVIEWS

" Achema " Jahrbuch 1937. It is a handbook which gives a detailed information and description of the 8th exhibition of German Chemical Engineering Plants, that took place this year at Frankfurt on the Main from the 2nd to the 11th of July. The products of 360 exibitors were displayed in seven halls that covered a total floor area of over 250.000 square feet and employed more than 29 miles of electrical wiring, which supplied light and power for the illumination and operation of the various exhibits, many of which were actually demonstrated to show the working of the full-size plants in service.

The book opens with the history of the " Achema " which was started in 1920 in a much more modest form, and has since been held from time to time in the more important towns of Germany in ever-increasing dimensions. This development is vividly explained by the help of diagrams and graphs, and then follows a detailed account of the various exhibits displayed in the last exhibition, classified under the following heads :

(1) Scientific laboratory apparatus and industrial equipments.
(2) Metallic and non-metallic apparatus, machines and vessels, and their starting materials.
(3) Artificial substances, their manufacture, manufacturing processes and plants.
(4) Complete manufacturing plants for the production of chemicals and allied substances. Workshop appliances and the fabrication of chemical plants.
(5) German artificial fibres : their production and utilisation in the industries.
(6) Contemporary Scientific Journals and Periodicals of Germany.

The most striking feature of this exhibition was the library, as well as a series lectures on Chemical Engineering, that were made available to intending members of the German Chemical, and Engineering Societies, and to *bona fide* students of the various German Universities.

The book is not only of considerable value as a guide to the visitors, but the detailed descriptions of the most up to date machineries and plants, together with the numerous technical advertisements incorporated into it, have made it a valuable book of reference, particularly to those who did not have the good fortune of visiting the exhibition itself.

C. B.

Dechema Monographien, Band 9. The ninth volume of the "Dechema" monographs, contains eight papers (Nos. 81-88), on three general subjects, *viz.*, "Researches on Chemical Engineering" (three papers), "Electro-thermics in Chemical Technology" .(four papers), and "Separation of gases in Technical Filtration Processes" (one paper). All these papers were previously published in the ninth and tenth volumes of the "Chemische Fabrik" during 1936 and 1937, and represent a selection from all the papers published therein in the respective fields.

The book begins with an article by P. Duden, which describes the work done by the "Dechema" during the last 10 years, with a brief history and the present position of the same, and elucidates the relation between chemists and engineers as well as the part expected to be played by Chemical Engineers, in industrial enterprises.

The special feature of the articles are the minimum mathematical considarations on the one hand, combined with the maximum amount of practical details of the respective problems and their solutions. The articles are profusely illustrated which adds to their interesting and helpful aspects. The volume is of particular utility to chemical engineers interested in the above subjects.

C. B.

THE CONSTITUENTS OF *DIDYMO-CARPUS PEDICELLATA*. PART I. ISOLATION OF A NEW SERIES OF COLOURING MATTERS.

By Salimuzzaman Siddiqui.

Didymo-carpus Pedicellata, N. O. *Gesneriaceae*, (Hindi, Pathar Phori : Sanskrit, Shila-Pushp ; Persian, Berg-i-Sang) is a small herbaceous plant found in the subtropical western Himalayan regions from Chamba to Kumaon at an altitude of 2 500-5,500 ft. The stem is nearly absent, sometimes upto 1½″ long, and carries two or three pairs of opposite, glabrous, cauline leaves. The dry leaves have a characteristic spicy odour and appear dusted with reddish colouring matter They are highly reputed in the indigenous medicine as a cure for kidney and bladder stones but the herb is not mentioned in Dymock's " Pharmacographica Indica " or Wehmer's " Pflanzenstoffe (Ed, 1930)." and no chemical investigation of it appears to have been so far undertaken.

As a result of the present investigation the following well-defined crystalline products have been isolated and characterised,

1. Pedicin, $C_{18}H_{18}O_6$: $C_{14}H_7 \cdot CO(OMe)_3\ (OH)_2$, m. p. 145°, bright orange-red elongated rectangular plates (yield, 1·0%).

2. *iso*Pedicin, $C_{18}H_{18}O_6$, m.p. 105°, star-like aggregates of pale yellow prismatic rods and needles (yield, 0·4%).

3. Pedicinin, $C_{16}H_{12}O_6$: $C_{15}H_8O_4(OH)(OMe)$, m.p. 203°, carmine red aggregates of stout rods and needles (yield, 0·3%).

4. Pedicellin, $C_{20}H_{22}O_6$: $C_{15}H_7O(OMe)_5$, aggregates of colourless rectangular plates, m.p. 98° (yield, 1·0%).

The yields given above are the maximum noted in three samples worked and are based on the weight of air-dried, powdered leaves. *iso*Pedicin could be isolated from only one of these samples in which the yields of pedicin and pedicinin were considerably lower than the maximum (about 0·5 and 0·1% respectively). The yield of pedicellin did not appreciably vary in the different samples. Stocking the drug for a longer period was found to materially lower the yields of all the crystalline products. The molecular formulae, noted above, have been fixed on the basis of C, H, methoxyl and M. W. values. On the basis of C, H and M. W. estimations pedicellin could also be given the formula $C_{23}H_{24}O_7$ but its methoxyl value definitely points to the lower formula. Pedicin, on the other hand, gave abnormally low M. W. values by cryoscopic and ebullioscopic methods, and also after Rast, but the C_{16}-formula for it was indicated by the values found for its single methoxyl group, and definitely established by the C, H and N values for its ammonium salt, $C_{16}H_{11}O_6, NH_4$, and the estimation of barium in its basic barium salt, $C_{16}H_{11}O_6,BaOH$.

The principal colouring matter, pedicin, which has been more fully investigated, was found to give a phenylhydrazone, showing the presence of a keto group in its molecule. It gave colouration with ferric chloride, was soluble in dilute caustic alkalies, insoluble in sodium carbonate and gave a water-insoluble lead salt. The presence of a phenolic hydroxyl in it is thus indicated. It also yielded a di-benzoyl derivative, whereby all the oxygen atoms in its molecule are accounted for as expressed in the formula noted for it above. It is unsaturated to bromine and could be reduced with Zn and HCl to a colourless hydro-derivative, whose analysis, however, indicates some other changes also, apart from the reduction of the double bond. In contrast to pedicin, pedicinin failed to give a phenylhydrazone, gave only a monoacetyl derivative and was soluble in dilute sodium carbonate solution. A discussion on the constitution of these products, which appear to be chalkone derivatives, will form part of a subsequent communication.

Apart from the products isolated and described in the present paper, an essential oil was also separated (yield, about 1·8%), which will be dealt with in a separate paper along with further constituents of the drug.

EXPERIMENTAL.

The drug was especially collected and supplied by the Himalayan Drug Company, Dehra Dun and kindly identified by Mr. C. E. Parkinson, the Botanist of the Forest Research Institute, Dehra Dun, to whom the author feels deeply indebted.

After preliminary investigations for finding out the best method for extracting the various constituents of the drug, 4 kg. of the air-dried, glandular leaves were coarsely powdered and extracted with ether in a modified Soxhlet apparatus. The ethereal extract was concentrated to a small volume (about 1 litre) and allowed to stand at the ordinary temperature for several days, when a bright orange coloured crystalline powder (50 g.) forming the major portion of the colouring matter contained in the leaves, separated out ; 18 g. of the crude colouring matter were further obtained on extraction of the ethereal mother liquors with dilute caustic soda solution, acidifying the alkaline solution with hydrochloric acid and cooling the ethereal extract of the acidic portion thus obtained. The original ethereal layer, containing the neutral matter insoluble in caustic soda, was acidified with hydrochloric acid, washed with water, dried over sodium sulphate, concentrated to a small volume and kept in the cold, when a large quantity of a nearly colourless crystalline product (crude pedicellin) separated out, the mother liquors yielding a further quantity of it on treatment with petroleum ether. The highly odorescent dark green residue, obtained on removing the solvent from the final filtrate from this product, was subjected to steam distillation. The non-volatile residue was extracted with ether and again separated into acidic and neutral fractions as stated above, when the neutral portion yielded through ether and petroleum ether mixture a further quantity of the crystalline neutral product (total yield, about 40 g.). The light greenish yellow product of steam distillation (yield 70 g. ; 1·8% on the wt. of the dry leaves) will be taken up, along with the constituents of the acidic mother liquors of the colouring matter and the mother liquors of crystalline neutral product, in a subsequent communication.

68 G. of the crude colouring matter were repeatedly extracted with ethyl acetate. Through alternate fractional crystallisation of the ethyl acetate soluble portion from benzene and ethyl acetate, 45 g. of pure pedicin (m.p. 145°) were finally obtained. The portion insoluble in ethyl acetate gave on repeated crystallisation from chloroform 11 g. of pedicinin (m.p. 203°) as a carmine-red, silky, crystalline product. No pedicine was obtained in this working. In a subsequent working of 500 g. of a fresh sample of the leaves, the mother liquor from pedicin gave 1·8 g. of *iso*pedicin on repeated crystallisation of the fraction soluble in dilute ammonia (ca. 5%) from a mixture of ethyl acetate and ether, as a pale yellow crystalline product showing the end m.p. 105°. The crude neutral matter referred to above (40 g.) gave 30 g. of pedicellin on repeated crystallisation from ether, as a colourless, crystalline product finally melting at 98°.

Characterisation of the Constituents.

Pedicin ($C_{18}H_{18}O_6$).—Pedicin is fairly soluble in alcohol and chloroform, less so in ethyl acetate and benzene, sparingly soluble in ether and nearly insoluble in petroleum ether. It dissolves in dilute caustic soda and fairly concentrated ammonia to a deep brownish red solution with a violet colour but not in sodium carbonate, and gives an amorphous dirty red precipitate with lead acetate in alcoholic solution. Its alcoholic solution gives an evanescent greenish blue colouration with ferric chloride quickly changing to pale yellow which then slowly develops into deep red and later reddish brown. It crystallises from organic solvents in bright orange-red, elongated, rectangular plates, m.p. 145°. It gives a reddish violet colouration with caustic soda and a deep red solution with concentrated sulphuric acid. [Found : C, 65.4 ; H, 5·3 ; OMe (after Zeisel), 27·2 ; M.W. (cryoscopic in phenol), 315 ; (after Rast), 328. $C_{18}H_{18}O_6$ requires C, 65·5 ; H, 5·5 ; OMe (for 3 methoxyls), 28·1 per cent ; M.W. 330 ; $C_{21}H_{20}O_7$ requires C, 65·1 ; H, 5·2 ; OMe (for 3 methoxyls), 24·2, (for 4 methoxyls), 32·2 per cent ; M.W., 384].

The Phenylhydrazone ($C_{18}H_{16}O_5$: N·NH·C_6H_5).—Pedicin (0·5 g.) was heated with phenylhydrazine (0·5 c.c.) on a water-bath and glacial acetic acid (2 c.c.) added to the light red solution. After further heating for about 10 minutes in the course of which the colour deepened, water was added to the reaction mixture when a reddish pasty mass separated out which was well washed with water. On agitating it with a little hot alcohol a straw coloured silky, crystalline product resulted, which was filtered, washed with alcohol and dried (yield 0·3 g., 50% of theory). The phenylhydrazone, thus obtained, took on a greenish tinge on heating in solvents. It is very sparingly soluble in ether, fairly soluble in alcohol from which it crystallises in bundles of slender needles, m.p. 165-67°. (Found after drying at 100° in *vacuo* over P2O_5 : C, 68·6 ; H, 5·8. $C_{24}H_{24}O_5N_2$ requires C, 68·6 ; H, 5·7 per cent).

The deep red filtrate from the phenylhydrazone gave a carmine-red, nitrogenous crystalline product, m.p. 190°, which will be described and discussed in a subsequent communication. The respective yields of the two crystalline products obtained through the action of phenylhydrazine on pedicine vary with the exact conditions employed, particularly with the duration of heating. The method given above was found to be most favourable for the regular phenylhydrazone (m.p. 165-67°).

Dibenzoylpedicin [$C_{18}H_{16}O_6$·$(C_6H_5CO)_2$].—Pedicin (0·3 g.) was dissolved in pyridine (5 c.c.) and benzoyl chloride (1·2 c.c.) was slowly added to the deep red solution with good cooling and stirring, whereby the colour lightened to pale orange and a white crystalline mass separated. After allowing the reaction mixture to stand for about an hour in the course of which the colour began to deepen, it was diluted with water and shaken up with a mixture of ethyl acetate and benzene. The light red benzene layer was well washed with water, dilute acetic acid and again with water, dried over sodium sulphate, filtered and concentrated, when pedicin benzoate crystallised out in colourless, short, scattered rods, which on recrystallisation from benzene melted at 181-83°. The mother liquors gave a further crop of crystals, m.p. 181°, (total yield 0·3 g., 60% of theory). It is sparingly soluble in ether and petroleum ether, fairly soluble in alcohol, ethyl acetate and benzene and yields the original colouring matter and benzoic acid on warming with alcoholic caustic potash for 5-10 minutes on the water-bath. (Found after drying at 100° in *vacuo* over P_2O_5 : C, 71·1 ; H, 4·8. $C_{32}H_{26}O_8$ requires C, 71·4 ; H, 4·8 per cent).

Dibenzoylpedicin was also obtained through benzoylation with caustic soda and benzoyl chloride, but the yields by this method were poorer and the isolation of the pure product more difficult.

Reduction of Pedicin.—A solution of pedicin (0·3 g.) in glacial acetic acid was shaken up in a small separating funnel with hydrochloric acid (10%, 1 c.c.) and ether (10 c.c.) with addition of small quantities of zinc dust till the original bright red colour had disappeared and a pale straw coloured ethereal solution was obtained. The ethereal layer was well washed with water and concentrated after drying, when the hydro product separated out as a straw coloured crystalline mass, which was fairly soluble in alcohol and ethyl acetate, less so in ether, sparingly soluble in petroleum ether, and on recrystallisation from ether melted at 211°. (Found after drying in *vacuo* over P_2O_5 : C, 64·6 ; H, 5·9.$C_{18}H_{20}O_6$ requires C, 64·5 ; H, 5·0. $C_{18}H_{22}O_6$ requires C, 64·7 ; H, 4·5 per cent).

iso*Pedicin* ($C_{18}H_{18}O_6$).—*iso*Pedicin is readily soluble in alcohol and ethyl acetate, less so in ether, very sparingly in petroleum ether. It dissolves in dilute ammonia and is precipitated from the ammoniacal solution by hydrochloric acid. It crystallises from organic solvents in aggregates of pale yellow prismatic rods, m.p. 105°. It gives a deep red solution with concentrated sulphuric acid and on adding ferric chloride to its alcoholic solution it slowly develops a deep red colouration which later turns reddish brown. In contrast to pedicin it appeared to be saturated to bromine in the cold. (Found after drying at 50° in *vacuo*: C, 65·4 ; H, 5·5. $C_{18}H_{18}O_6$ requires C, 65·5 ; H, 5·5 per cent).

Pedicinin ($C_{16}H_{12}O_6$.).—Pedicinin is fairly soluble in alcohol and chloroform in the hot, sparingly in benzene, nearly insoluble in ethyl acetate and ether, insoluble in petroleum ether and crystallises in aggregates of carmine-red, stout rods and needles, m.p. 203°. It dissolves in dilute caustic soda, ammonia and also in sodium carbonate forming orange-red to deep red solutions and gives an amorphous dirty red precipitate with lead acetate in alcoholic solution. Like pedicin and *iso*pedicin it gives a deep red solution with concentrated sulphuric acid. On adding ferric chloride to its alcoholic solution it gives in contrast to them an *immediate* deep reddish brown colouration. [Found after drying at 100° in *vacuo* over P_2O_5 : C, 64·1 ; H, 4·1 ; OMe (after Zeisel), 10·3 ; M. W. (cryoscopic in phenol), 172, (ebullioscopic in benzene), 150; (after Rast), 227. $C_{16}H_{12}O_6$ requires C, 64·0; H, 4·1; OMe (for 1 methoxyl), 10.3 per cent; M. W., 200).

The Ammonium salt ($C_{16}H_{11}O_6$, NH_4) was obtained on passing dry ammonia gas through a chloroform solution of pedicinin as a dark red powder in a quantitative yield. It is easily soluble in water forming a red solution and sparingly soluble in alcohol from which it crystallises in dark red stout rods, m.p. 149°, while the uncrystallised salt melts at 145°. (Found after drying at 100° in *vacuo* over P_2O_5: C, 60·23; H, 5·38; N. 4·60. $C_{16}H_{15}O_6N$ requires C, 60·56; H, 4·73; N, 4·41 per cent).

The Barium salt ($C_{16}H_{11}O_6BaOH$) was obtained on adding an aqueous solution of barium hydroxide to an aqueous solution of the ammonium salt as a dark red semi-crystalline powder which was insoluble in the usual solvents and did not melt. (Found: Ba, 30·3, 30·7. $C_{16}H_{12}O_7$ Ba requires Ba, 30·3 per cent).

Monoacetyl pedicinin ($C_{16}H_{11}O{\cdot}OC{\cdot}CH_3$). — Pedicinin (0·2 g.) was heated on the water-bath with acetic anhydride (6 c.c.) and a crystal of fused sodium acetate added to the solution when a temporary darkening of colour ocurred, which later on changed to orange-yellow. Water was then added to the reaction mixture. The yellowish oily layer, thereby obtained, later turned into a light yellow crystalline mass which, on recrystallisation from ethyl acetate, gave the acetyl derivative as light yellow, scattered, prismatic rods, m.p. 175°, in a nearly quantitative yield. (Found after drying at 100° in *vacuo*: C, 63·3; H, 4·2. $C_{18}H_{14}O_7$ requires C, 62·9; H, 4·1 per cent).

Pedicellin ($C_{20}H_{22}O_6$).—Pedicellin is fairly soluble in alcohol and ethyl acetate, sparingly soluble in ether, nearly insoluble in petroleum ether, and crystallises from all these solvents in aggregates of rectangular plates, m.p. 98°. It is insoluble in alkali and gives a deep red colouration with concentrated sulphuric acid. [Found after drying at 50° in *vacuo*: C, 67·2; H, 6·3; M.W. (after Rast), 312, (cryoscopic in phenol) 469; Me (after Zeisel's method), 43·0. $C_{20}H_{22}O_6$requires C, 67·0; H, 6·1; M.W. 358; OMe (for 5 OMe), 43·0 per cent. $C_{23}H_{24}O_7$ requires C, 67·0; H, 6·2; M.W., 421; OMe (for 5 methoxyls), 37·6; (for 6 methoxyls), 45·1 per cent). It does not form an acetyl or a benzoyl derivative by the usual methods and apparently does not contain a hydroxyl group in its molecule.

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STUDIES IN INDIGOID DYES. PART II.

By Sisir Kumar Guha.

In the acenaphthenequinone series Martinet's rule (*Rev. Gen. Mat. Col.*, 1921, **25**, 17) is applicable to 2-thionaphthene-acenaphthylene-indigos (Bezdzik and Friedlander, *Monatsh.*, 1908, **29**, 386 ; E.P. 344/08 ; G. P. 226244 ; Mayer and Schönfelder, *Ber.*, 1922, **55**, 2972 ; G. P. 213504 ; E. P. 20003/08 ; Guha, *J. Indian Chem. Soc.*, 1932, **9**, 423) and in the isatin series to 3-indole-2′-thionaphtheneindigos (Bezdzik and Friedlander, *Monatsh.*, 1908, **29**, 376 ; E. P. 17162/06 ; G. P. 241327 ; E. P. 19158/07 ; G. P. 277358) as far as one Me group in the thionaphthene nucleus of the molecule is concerned (Guha, *J. Indian Chem. Soc.*, 1933, **10**, 679 ; 1936, **13**, 94 ; Guha and Basu-Mallik, *ibid.*, 1934, **11**, 395 ; Guhà, *ibid.*, 1937, **14**, 240). The dyestuffs obtained by the condensation of α-chloride of isatin and 6-methyl-3-hydroxythionaphthene and 5-methyl-3-hydroxythionaphthene respectively and their derivatives may also be compared. (F. P. 693903 of 14/4/1930 ; *Chem Zentrl.*, 1931, **102**, I, 2944 ; A.P. 1850758 of 10/12/1930. *Chem. Zentrl.*, 1932, **103**, II, 1374).

In another communication (Guha, *J. Indian Chem. Soc.*, 1935, **12**, 659) 5-methyl detivatives of benzylidene-2-thionaphthene (Auwers and Arndt, *Ber.*, 1909, **42**, 543) and its various substituted products and also that of bis-2-thionaphthene-ethyleneindigo (Friedlander and Risse, *Ber.*, 1914, **47**, 1924) were studied. The object of this investigation was to obtain their corresponding 6-methyl derivatives and to examine if Martinet's rule holds good in the series as well having only one Me group in the thionaphthene part of the molecule of the compounds.

With this object in view, 6-methyl-3-hydroxythionaphthene (Friedlander, **9**, 589 ; Auwers and Thies, *Ber.*, 1920, **53**, 2293) was condensed with glyoxal, benzaldehyde, *p*-nitro-, and *p*-dimethylamino-benzaldehyde respectively and the corresponding dyestuffs obtained. Here those aldehydes only have been selected which gave rise to compounds of fairly prominent colours in the 5-methyl series (Guha, *loc. cit.*). The 6-methyl compounds described here resemble the corresponding 5-methyl derivatives in crystallising power, in solubility and in developing shades on wool and on cotton, unless mentioned otherwise in the experimental part. The colours, developed on wool and on cotton from the substances described in this part, are pronouncedly lighter in shade than those obtained from the corresponding 5-methyl compounds (Guha, *loc. cit.*) showing that Martinet's rule is also applicable to this series of compounds. A comparison of some of the colours on wool and on cotton obtained from the compounds of the two series is given below.

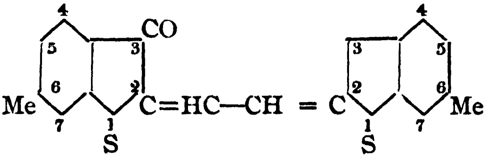
Names.	Dyeing shades on wool.	on cotton.
bis-2(6 Methyl)-thionaphthene-ethylene-indigo	Scarlet red	Deep scarlet-red
bis-2(5-Methyl)-thionaphthene-ethylene-indigo	Dark red	Violet-red
4′-Nitro-benzylidene-2-(6-methyl)-thionaphthene	Deep yellow	Yellowish orange
4′-Nitro-benzylidene-2-(5 methyl)-thionaphthene	Orange yellow	Light orange
4′-Dimethylaminobenzylidene-2-(6-methyl)-thionaphthene	Cinnabar red	Light pink
4′-Dimethylaminobenzylidene-2(5-methyl)-thionaphthene	Cinnabar red	Pink

2:3-Naphthoxythiophene (Friedlander and Woroshzow, *Annalen*, 1912, **388**, 18) was condensed with acenaphthenequinone and a blue-red dye was obtained. This dye on bromination gave a blue-red product (Schwz P. P. 107133-35 of 29/3/23. *Chem. Zentbl.*, 1925, **96**, **II**, 860). Later on Dutt (*Ber.*, 1934, **67**, 1326. *cf.* E. P. 209092 of 27/12/23) prepared the same mother compound and has described it to be rose-violet. The present author has condensed 3-chloro-, 3-bromo-, and β-methoxyacenaphthenequinone with 2:3-naphthoxythiophene respectively with a view to study the effect of different elements or groups on the colour of the mother compound and the corresponding dyes prepared. These are all red-violet substances, the methoxy derivative possessing the deepest shade of the three. They are sparingly soluble in acetic acid, amyl alcohol, and less so in alcohol, and are soluble in nitrobenzene They melt when heated above 305° and quickly volatilise evolving vapours of the respective substances. They dissolve in strong sulphuric acid with a green colour from which water reprecipitates the original substances. The halogenated products are reduced by alkaline hydrosulphite producing green vat from which the original dyes are reprecipitated by oxidation with air. The methoxy derivative could not be easily converted into a soluble vat. The dirty white colour developed, after repeated trial, on cotton from the alkaline vat turned light violet by atmospheric oxidation. [*cf.* 2-thionaphthene-8′-(1′-methoxy)-acenaphthylene-indigo, its 5-methyl and 6-methyl derivatives only. Staudinger, Goldstein and Schlenker, *Helv. Chim. Acta*, 1921, **4**, 342; Guha, *loc. cit.*].

EXPERIMENTAL.

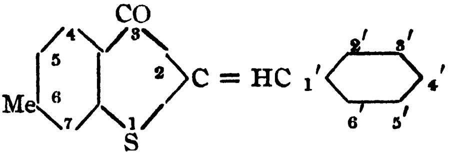
The *bis*-2(-6-methyl)-thionaphthene-ethyleneindigo and benzylidene-2-(6-methyl)-thionaphthenes described below were prepared in the same way as the corresponding 5-methyl compounds (Guha, *loc. cit.*).

bis-2-(6-*Methyl*)-*thionaphthene-ethyleneindigo.*



It was prepared from glyoxal sodium bisulphite (0·568 g.) in 15 c.c. of water and 6-methyl-3-hydroxythionaphthene (0·656 g.) in hot absolute alcohol (40 c.c.) and concentrated hydrochloric acid (10 c.c.). The dye (0·381 g.) crystallised from toluene in deep red shining needles, m.p. 300° (decomp.). It is soluble in chloroform, difficultly in benzene, toluene, and sparingly soluble in carbon tetrachloride and less so in petroleum ether. It dissolves in concentrated sulphuric acid with a green colour and dyes wool in pleasant scarlet red shades from an acid bath and cotton in deep scarlet red shades from a deep yellow vat. (Found : S, 18·71. $C_{20}H_{14}O_2S_2$ requires S, 18·28 per cent).

Benzylidene-2-(6-*methyl*)-*thionaphthene.*



It was obtained as yellow rectangular substance from benzaldehyde (0·424 g.) and 6-methyl 3-hydroxythionaphthene (0·656 g.) in hot absolute alcohol (10 c.c.) and concentrated hydrochlioric acid (2 c.c.). The product (0·839 g.) crystallised from dilute alcohol in silky long yellow rectangular crystals, m. p. 134-35°. It dyes wool in yellow shades from an acid bath. (Found: S, 12·46. $C_{16}H_{12}OS$ requires S, 12·69 per cent).

4′-*Nitro-benzylidene*-2-(6-*methyl*)-*thionaphthene* separated as yellowish-orange crystalline precipitate from *p*-nitrobenzaldehyde (0·453 g.) and 6-methyl-3-hydroxythionaphthene (0·492 g.) in 22 c.c. of hot absolute alcohol and concentrated hydrochloric acid (3 c.c.) The substance (0·738 g.) crystallised in long silky yellowish orange needles, m. p. 228-29°. It is moderately soluble in alcohol. The solution in concentrated sulphuric acid is purple. It dyes wool in deep yellow shades from acid bath and cotton in yellowish orange shades from an orange vat. (Found : S, 11·19. $C_{16}H_{11}O_3NS$ requires S, 10·77 per cent).

4′-Dimethylaminobenzylidene-2-(6-methyl)-thionaphthene.—A greenish yellow crystalline precipitate of the hydrochloride of the base was obtained by condensing *p*-dimethylaminobenzaldehyde (0·596 g.) and 6-methyl-3-hydroxythionaphthene (0·656 g.) in hot absolute alcohol (13 c.c.) and concentrated hydrochloric acid (1·5 c.c.) It gave on washing with dilute alcohol the red dye (0·985 g.). It crystallised from methyl alcohol in hexagonal iridescent prisms, m.p. 193°. It is soluble in petroleum ether. It dissolves in concentrated sulphuric acid with a violet red colouration. It dyes wool in cinnabar red shades and cloth in light pink colour from a faintly red vat. (Found: S, 11·13. $C_{18}H_{17}ONS$ requires S, 10·84 per cent).

2:3-*Naphthathiophene-8′-(3′-chloro)-acenaphthylene-indigo.*

The red-violet small needles, obtained from 3-chloro-acenaphthenequinone (0·649 g.) and 2:3-naphthoxythiophene (0·6 g.) in 70 c.c. of boiling glacial acetic acid and 4 c.c. of concentrated hydrochloric acid by heating for 15 minutes, were purified by heating with acetic acid and crystallised from nitrobenzene in beautiful clusters of long needles. It is difficultly soluble in pyridine, xylene, moderately soluble in chloroform. It dyes cotton in red violet shades from an alkaline hydrosulphite vat. (Found: Cl, 9·24. $C_{24}H_{11}O_2ClS$ requires Cl, 8·91 per cent).

2 : 3-*Naphthathiophene-8′-(3′-bromo)-acenaphthylene-indigo* was prepared from 3-bromoty-acenaphthenequinone (0·783 g.) and 2:3-naphthoxythiophene (0·6 g.) in 80 c.c. of boiling acetic acid and 4 c.c. of concentrated hydrochloric acid. The red-violet crystalline precipitate was purified and crystallised in the same way as the preceding compound. It possesses properties similar to the preceding compound. (Found : Br, 18·27. $C_{24}H_{11}O_2BrS$ requires Br, 18·05 per cent).

2 : 3-*Naphthathiophene-8′-(1′-methoxy)-acenaphthylene-indigo* separated as deep red-violet needles from *β*-methoxyacenaphthenequinone (1·06 g.) and 2:3-naphthoxythiophene (1 g.) in 130 c.c. of boiling glacial acetic acid and 10 c.c. of concentrated hydrochloric acid by heating for 30 minutes. The dye is soluble in pyridine, aniline, difficultly soluble in chloroform. It dyes cotton in light violet colour. (Found : S, 7·79. $C_{25}H_{14}O_3S$ requires S, 8·12 per cent).

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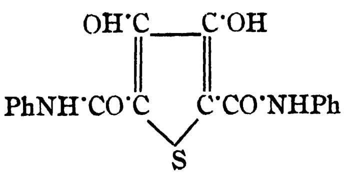
QUINOLINE DERIVATIVES. PART III.

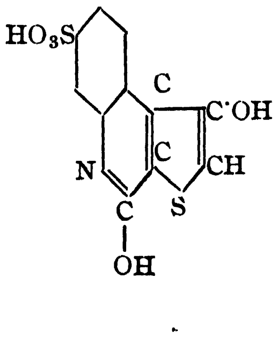
By Tejendra Nath Ghosh.

Many sulphur compounds have been suggested as useful antiseptics, but few have kept their place in therapeutics, the chief exception being ichthyol. The therapeutic value of ichthyol oils has been attributed to the presence of alkylthiophens (Scheibler, *Arch. Pharm.*, 1920, **258**, 84). The influence of the thiophen radicle in increasing the therapeutic activity has been demonstrated by Hartmann and Wybert (*Helv. Chim. Acta*, 1919, **2**, 60) who have replaced the phenyl group in the cinchophen molecule by the thiophen radicle and have found that the resulting product possesses marked antiphlogistic and analgesic properties.

In view of the above findings, it seemed of considerable interest to synthesise a compound in which the thiophen ring is fused with the quinoline residue. With this object in view, ethyl 3:4-dihydroxythiophen-2:5-dicarboxylate (Hinsberg, *Ber.*, 1910, **43**, 901) has now been allowed to react with aniline at 170-75°, when the dianilide (I) is obtained. When treated with strong sulphuric acid at 100°, the compound (I) furnishes the quinoline derivative (II).



(I)

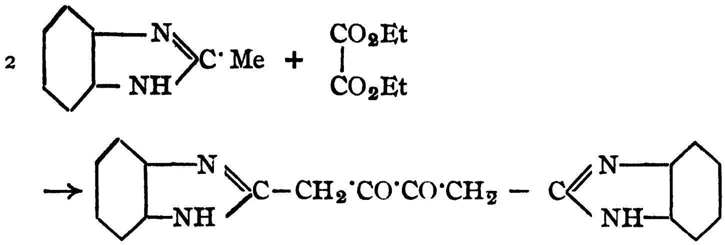


(II)

By boiling with concentrated hydrobromic acid (*cf.* Besthron and Jaegté, *Ber.*, 1894, **27**, 907), the sulphonic group in compound (II) could not be eliminated, only the corresponding hydrobromide being formed by this treatment. The compound (II) is, therefore, amphoteric, as it forms a hydrochloride or hydrobromide as well as a metallic salt. Further, it is interesting to note that the presence of a sulphonic group has been found to enhance the therapeutic activity of many organo-metallic compounds (*cf.* Solganal and Krysolgan, Freund, *Beitr. Klin. Wochenschr,* 1928, **68**, 606).

In order to form quinoline residues on both sides of the thiophen ring, action of phosphorus pentoxide on the compound (I) was tried, but without success. A similar difficuly in forming pyridine rings on both sides of a benzene nucleus has been encountered by Marckwald and Schmidt (*Annalen,* 1893, **274**, 367).

In recent years, an ideal antimalarial has been sought in glyoxalinoquinolines by Narang and Ray (*J. Chem. Soc.,* 1931, 976). It has been, therefore, thought worth while to synthesise a benziminazolylquinoline derivative so that its antimalarial properties may be studied. 2-Methylbenziminazole, in which there is a reactive methyl group (Mills and Smith, *J. Chem. Soc.,* 1922, **121**, 2724), has now been condensed with ethyl oxalate in presence of sodium ethoxide to yield the compound (III).



(III)

It was planned to utilise the compound (III) for the synthesis of *bis*-benziminazolylquinoline derivative, but the compound (III) could not be condensed with *o*-nitrobenzaldehyde under many conditions tried.

EXPERIMENTAL.

2:5-*Diphenylcarbamido*-3:4-*dihydroxythiophen* (I).—A mixture of ethyl 3:4-dihydroxythiophen-2:5-dicarboxylate (10·4 g.) and aniline (7·5 g.) was heated on an oil-bath at 160° for 30 minutes and at 170-75° for 2½ hours. The dark pasty mass was triturated with alcohol and the solid was then filtered and washed several times with alcohol. It crystallised from dilute pyridine in colourless needles, m.p. 292-93° (decomp., producing an intense eenish black colouration), yield 8·5 g. It is insoluble in glacial acetic acid and alcohol. It is soluble in cold alkali (the alkaline solution being coloured yellow) and precipitated by acids. It is unaffected by boiling with concentrated hydrochloric acid. A pyridine solution of the substance gives an intense greenish black colouration with ferric chloride. [Found : N, 7·96 ; S, 8·73 ; M.W. (by titration), 350. $C_{18}H_{14}O_4N_2S$ requires N, 7·90 ; S, 9·04 per cent. M.W., 354].

4-*Hydroxythiophen*-2:3(3′:4′)-2′-*hydroxyquinoline-sulphonic Acid* (II).—The above compound (I, 6 g.) was heated with concentrated sulphuric acid (30 c.c.) on an oil-bath at 100° for 3 hours. Effervescence was noticed in the reaction mixture, which was allowed to cool and poured into ice-cold water. The presence of aniline in the acid solution was confirmed by diazotisation and coupling with β-naphthol. The clear acid solution was treated with excess of sodium carbonate and filtered from slight pasty mass. The solution was next acidified with dilute hydrochloric acid, when a greenish white amorphous solid was obtained, which was twice crystallised from hot water (charcoal) in colourless plates, yield 1·5 g. It does not melt even at 310° and appears to be non-fusible. [Found : N (Kjeldahl), 4·72 ; S, 20·88 ; M.W. (by titration), 299. $C_{11}H_7O_5NS_2$ requires N, 4·71 ; S, 21·54 per cent. M. W., 297]. It is soluble in aqueous bicarbonate solution and precipitated by acids. It is insoluble in alcohol, acetic acid and other organic solvents. With pyridine it forms a salt, soluble in cold water. With ferric chloride, an aqueous solution of the substance gives a dark green colouration.

When the above compound is boiled for a few minutes with concentrated hydrobromic acid (*d* 1·38), it is converted into the corresponding hydrobromide (colourless rectangular plates, m.p. above 300°). It is insoluble in concentrated hydrobromic acid but readily soluble in cold water and on neutralisation with just the requisite quantity of sodium bicarbonate, the original acid (II) is obtained. Similarly the hydrochloride (colourless rectangular plates, m.p. above 300°) was obtained by boiling the substance with concentrated hydrochloric acid. With regard to the formation of hydrochloride, the compound (II) resembles the *cyclo*pentane-2′-hydroxyquinoline derivative of Dieckmann (*Annalen*, 1901, **317**, 91).

Condensation of Ethyl 1-N-*phenyl*-3:4-*dihydroxypyrrolidine*-2:5-*dicarboxylate with Aniline*.—This pyrrolidine derivative, which is similar in constitution to the above thiophen derivative of Hinsberg, was prepared according to the method of Johnson and Bengis (*J. Amer. Chem. Soc.*, 1911, **33**, 745). Its condensation with aniline was tried according to the method followed in the preparation of (I), but no reaction was observed. The great stability of the carbethoxy groups in this pyrrolidine derivative towards hydrolysing agents has been observed by Mouilpied (*J. Chem. Soc.*, 1905, **87**, 435) and their inertness towards aniline may be likewise explained.

1:4-*Dibenziminazolyl diacetyl* (III).—Sodium (2·3 g.) was dissolved in absolute alcohol (100 c.c.) and to the cold solution 2-methylbenziminazole (13·2 g.) was added. To the clear thick solution, ethyl exalate (7·3 g.) was then slowly added with stirring, when the reaction began with evolution of heat. The reaction mixture was allowed to stand for one day with occasional stirring, when the whole solution solidified. The mass was then treated with large quantity of cold water and extracted with ether. The aqueous solution, on acidification with excess of dilute hydrochloric acid, yielded a precipitate which was washed with aqueous sodium bicarbonate solution and water. It crystallised from hot water in beautiful colourless slender needles, m.p. above 300°, yield 3 g. (Found: N, 17·42. $C_{18}H_{14}O_2N_4$ requires N, 17·61 per cent). The same compound is obtained if 2-methyl-benziminazole (1 mol.) is allowed to react with ethyl oxalate (1 mol.). It is soluble in cold alkali and precipitated by acids.

The above compound is insoluble in most of the organic solvents except pyridine. Its condensation with *o*-nitrobenzaldehyde was tried in acetic anhydride suspension in presence of fused sodium acetate, but without success. The condensation was next tried in pyridine solution in presence of a few drops of piperidine (*cf.* Dutt, *J. Indian Chem. Soc.*, 1924-25, **1**, 297) and although the solution was boiled under reflux for a considerably long time, the expected condensation could not be effected.

My thanks are due to Professor P. C. Guha for his kind interest in this investigation. My thanks are also due to the Lady Tata Memorial Trust for the award of a scholarship.

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PECHMANN'S CONDENSATION OF METHYL β-RESORCYLATE AND β-RESORCYLIC ACID WITH ETHYL ACETOACETATE.

By R. C. Shah, S. M. Sethna, Bhawani Charan Banerjee and
Duhkhaharan Chakravarti.

Clayton generalised that negative substituents like nitro, carboxyl and carbethoxyl inhibit Pechmann's coumarin-condensation. 2-Nitro- and 4-nitroresorcinols, however, readily condense with ethyl acetoacetate (Chakravarti and Ghosh, *J. Indian Chem. Soc.*, 1935, **12**, 622; Chakravarti and Banerjee, *ibid.*, 1937, **14**, 37).

We find that methyl β-resorcylate and β-resorcylic acid smoothly condense with ethyl acetoacetate in the presence of sulphuric acid, the former giving a mixture of methyl 7-hydroxy-4-methylcoumarin-6-carboxylate and the correspooding carboxylic acid and the latter the free acid. The constitutions of the acid and the ester follow from the decarboxylation of the acid to known 7-hydroxy-4-methylcoumarin.

The condensation of methyl β-resorcylate was also carried out with phosphoryl chloride, phosphoric anhydride and hydrogen chloride as condensing agents, the same coumarin ester being obtained in low yields. It is noteworthy that the condensation proceeds differently in the presence of aluminium chloride the main product being a 5-hydroxy-coumarin, methyl 5-hydroxy-4-methylcoumarin-6-carboxylate (Sethna, Shah and Shah, *Current Science*, 1937, **6**, 94).

β-Resorcylic acid also condenses with malic acid in the presence of sulphuric acid with the formation of 7-hydroxycoumarin-6-carboxylic acid (*cf.* Arima, *Bull. Chem. Soc. Japan*, 1929, **4**, 113). Methyl β-resorcylate gives the same acid, the ester being completely hydrolysed at the temperature required for the condensation.

EXPERIMENTAL.

Methyl 7-Hydroxy-4-methylcoumarin-6-carboxylate and 7-Hydroxy-4-methylcoumarin-6-carboxylic Acid.

Concentrated sulphuric acid (80%, 30 c. c.) was added to a mixture of methyl β-resorcylate (5 g.) and ethyl acetoacetate (4·5 g.). The mixture after standing overnight, was added to cold water. The yellowish solid (7-8 g.) was collected, washed with water and then treated with excess of saturated sodium bicarbonate solution. The insoluble solid consisting of the coumarin ester was filtered and the filtrate was acidified when the free acid was precipitated as a granular solid.

The coumarin ester crystallised from alcohol in shining colourless needles, m. p. 212-14°, yield 3 g. (Found : C, 61·6 ; H, 4·3. $C_{12}H_{10}O_5$ requires C, 61·5 ; H, 4·3 per cent). The ester is moderately soluble in methyl and ethyl alcohols, acetone and chloroform, but very sparingly in benzene and water. It gives a violet colouration with alcoholic ferric chloride and dissolves in caustic soda with difficulty, the alkaline solution having a strong blue fluorescence.

The *acetyl* derivative, prepared by refluxing the ester (0·3 g.) with acetic anhydride (1 c. c.) and 2-3 drops of pyridine for 2 hours, crystallised from rectified spirit in needles, m. p. 171-73°, yield 0·15 g. (Found : C, 60·6 ; H, 4·4. $C_{14}H_{12}O_6$ requires C, 60·9 ; H, 4·3 per cent).

The *benzoyl* derivative, prepared by heating with benzoyl chloride for 1 hour at 100° in pyridine solution, crystallised from hot xylene in shining buttons, m. p. 173-74°. (Found: C, 67·3 ; H, 4·2. $C_{19}H_{14}O_6$ requires C, 67·4 ; H, 4·2 per cent).

The *methyl ether* was prepared by refluxing for 20 hours the ester (0·5 g.) dissolved in acetone (50 c. c.), fused potassium carbonate (1 g.) and methyl iodide (3 c. c.). It was crystallised from rectified spirit as clusters of tiny needles, m. p. 186-88°, yield 0·4 g. (Found : C, 62·82 ; H, 4·95. $C_{13}H_{12}O_5$ requires C, 62·9 ; H, 4·83 per cent). It is insoluble in alkali and does not give a ferric chloride colouration.

The coumarin acid crystallised from alcohol in short faintly coloured needles, m. p. 284-85°, yield 2 g. (Found : C, 59·8 ; H, 3·7. $C_{11}H_8O_5$ requires C, 60·0 ; H, 3·6 per cent). It is only sparingly soluble in alcohol and the alcoholic solution gives a dark violet colouration with ferric chloride. It dissolves in alkali to a pale yellow solution with intense blue fluorescence. Attempts to prepare acetyl and benzoyl derivatives by the usual methods were unsuccessful.

The same acid was obtained by the hydrolysis of the coumarin ester preferably by cold alkali. 0·5 G. of the ester was kept in contact with caustic soda solution (20 c. c., 10 %.) for 3 days when the ester went completely into solution. Acidification yielded the acid, identical with the acid described above. The acid was also obtained by hydrolysis with boiling acetic acid-hydrochloric acid or hot acetic acid—sulphuric acid or cold concentrated sulphuric acid, *Decarboxylation of 7-Hydroxy-4-methylcoumarin-6-carboxylic Acid.*—The acid (0·4 g.) and water (25 c.c.) were heated together in a sealed tube at 180° for 7 hours. The decarboxylated product, which had separated in thin shining needles with a brownish tinge, was crystallised from dilute alcohol in needles, m. p. 185-86°, not depressed by admixture with an authentic specimen of 7-hydroxy-4-methylcoumarin, yield quantitative. The acid can also be conveniently decarboxylated by gently heating the substance in a test tube, until effervescence ceases.

Condensation of β-Resorcylic Acid with Ethyl Acetoacetate.—Concentrated sulphuric acid (20 c.c.) was added to a mixture of β-resorcylic acid (5 g.) and ethyl acetoacetate (5 g.) when heat was evolved and the mixture turned brownish. After keeping overnight, the mixture was heated on a boiling water-bath for 2 hours, cooled and poured into water. The precipitated solid was treated with saturated sodium bicarbonate solution when most of it dissolved, leaving a small amount of residue which when crystallised from alcohol had m.p. 185-86° and was found to be 7-hydroxy-4-methylcoumarin. The sodium bicarbonate extract on acidification with concentrated hydrochloric acid, gave a yellowish coloured precipitate, which was collected and crystallised from alcohol or glacial acetic acid in colourless needles, m.p. 284-85° identical with the acid described above, yield 1·5 g.

Condensation of Methyl β-Resorcylate with Ethyl Acetoacetate in presence of (i) Phosphoryl chloride (ii) Phosphoric anhydride and (iii) Hydrogen chloride.

(*i*) To a mixture of methyl β-resorcylate (4 g.) and ethyl acetoacetate (3·5 g.) phosphorus oxychloride (7 g.) was added and the reaction mixture heated on a boiling water-bath for 1 hour. Water was added to the brown pasty mass. On keeping overnight in a frigidaire dark-brown semi-solid mass was obtained. This was dissolved in rectified spirit (charcoal). On keeping black tarry mass came down which was rejected. The clear solution was then concentrated and kept in a frigidaire when faint yellow coloured needles separated, m.p. and mixed m.p. with the compound prepared by using sulphuric acid, 212-14°, yield 0·3 g.

(*ii*) Methyl β-resorcylate (5 g.) and ethyl acetoacetate (4·5 g.) were mixed together and phosphorus pentoxide (5 g.) added. The reaction mixture was heated on a boiling water-bath for about 45 minutes. On cooling water was added and ths semi-solid mass obtained crystallised from rectified spirit as needles, m.p. and mixed m.p. with the compound prepared by sulphuric acid method, 212-14°, yield about 0·2 g.

(*iii*) Methyl β-resorcylate (5 g.) and ethyl acetoacetate (4·5 g.) were dissolved in sufficient cold absolute alcohol and dry hydrochloric acid gas passed through the cooled solution for 2½ hours. It was then left overnight when white needles separated. Water was added to precipitate the product completely which was then crystallised from rectified spirit colourless shining needles, m.p. and mixed m. p. with the compound prepared by sulphuric acid method, 212-14°, yield 1·3 g.

7-Hydroxycoumarin-6-carboxylic Acid.—Concentrated sulphuric acid (20 c.c.) was added to a mixture of β-resorcylic acid (5 g.) and malic acid (4·5 g.) and the mixture left overnight. After heating at 100° for 3-4 hours, it was poured into water. The pasty mass, which separated, solidified on keeping overnight in a frigidaire. It crystallised from alcohol in needles, m.p. 268°-69°. Arima (*loc. cit.*) gives m.p. 244°-260° according to rate of heating. (Found: C, 53·4; H, 3·5. Calc. for $C_{10}H_6O_5$, H_2O : C, 53.6; H, 3·4 per cent).

The acid dissolves in sodium bicarbonate forming a sparingly soluble sodium salt which immediately separates. It dissolves in alkali and concentrated sulphuric acid with a strong blue fluorescence.

The acid on decarboxylation by gentle heating gave 7-hydroxy coumarin, identified by direct comparison with an authentic specimen. The same acid was obtained by keeping a mixture of methyl β-resorcylate (5 g.), malic acid (4·2 g.) and concentrated sulphuric acid (15 c.c.) overnight, and then heating at 100° for 2 hours.

The analyses recorded are micro-analyses by Dr. Schoeller.

Further work on the condensation of other phenol-carboxylic acids and their esters with β-ketonic esters is being carried out by two of the authors (R.C.S. and S.M.S.).

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ASCORBIC ACID OXIDASE FROM THE WHITE GOURD (*BENINCASACRIAPRA*).

BY BAIDYANATH GHOSH AND B. C. GUHA.

The preparation of an ascorbic acid oxidising enzyme from cabbage was described by Szent-Györgyi (*Science,* 1930, **72,** 125; *J. Biol. Chem.*, 1931, **90,** 385). Tauber, Kleiner and Mishkind (*J. Biol. Chem.*, 1935, **110,** 211) prepared an enzyme from Hubbard squash also capable of oxidising ascorbic acid reversibly and studied the properties of their preparation in some detail. Srinivasan (*Biochem. J.*, 1936, **30,** 2077) prepared the same enzyme from the Indian drumstick. The distribution of the enzyme in plant and animal tissues was investigated by Chakraborty and Guha (*Indian J. Med. Res.*, 1937, **24,** 839), who found the animal tissues to be practically devoid of the oxidase and observed that the cucumber and the white gourd (Bengali, *chalkumro*) were the richest sources among the plant materials investigated. An enzyme preparation from cucumber was obtained by Chakraborty (*private communication*) and has been described by Johnson and Zilva (*Biochem. J.*, 1937, **31,** 438).

The present work was undertaken in order to obtain an ascorbic acid oxidase preparation from the white gourd (*Benincasacriapra*) and also to obtain information about its properties, the conditions of its activity and its specificity.

Fuller information about the properties of the ascorbic acid oxidase has become necessary particularly because it has been recommended as a reagent for the estimation of ascorbic acid (Tauber *et al*, *J. Biol. Chem.*, 1935, **110,** 559) and its use has also been found to lead to more specific results in the estimations carried out in this laboratory which will be published later.

EXPERIMENTAL.

Preparation of the Enzyme.—The method followed was approximately that of Tauber (*et al loc. cit*). White gourd was minced in a hand mincer. 200 G. of minced plant tissue were shaken for 5 minutes with 600 c.c. of 30% alcohol and filtered. The p_H of the alcoholic filtrate was 5·0. To the alcoholic extract an equal volume of acetone was added and the precipitate quickly removed. It was dissolved in 80 c. c. of distilled water and again precipitated with an equal volume of acetone. The enzyme was purified by repeating the process two or three times and then dried in a vacuum desiccator. It was light grey in colour.

On repeated purification the enzyme preparation becomes much lighter in colour. It appears to be fairly stable if stored in a vacuum desiccator at room temperature (26-30°). It takes some time to go into aqueous solution and for use the aqueous solution is centrifuged clear from a small residue. The aqueous solution lasts about a week if preserved with a drop or two of toluene in a stoppered vessel in a refrigerator. For the following experiments the solid enzyme preparation obtained from 200 g. of white gourd was dissolved in 80 c.c. of water.

A. Activity of the Enzyme at different p_H.

The activity of the enzyme was determined by the amount of ascorbic acid oxidised by the enzyme solution using 0·5 mg. of ascorbic acid as the substrate at 40° for 5 minutes at different p_H. After the period of incubation the enzyme activity was stopped by the addition of 1 c.c. of 2% sulphuric acid and titration was carried out with 2:6-dichlorophenol-indophenol according to the method previously described (Ghosh and Guha, *J. Indian Chem. Soc.*, 1935, **12**, 30).

TABLE IA.

Citrate phosphate buffer (McIlvaine).

The mixture consisted of citrate phosphate buffer (1 c.c.), enzyme solution (2 c.c.) and ascorbic acid (1 c.c., 0·5 mg).

p_H.	Amount of ascorbic acid oxidised.	Percentage of oxidation.
4·0	0·08 mg.	16%
4·4	0·10	20
5·2	0·20	40
5·4	0·20	40
5·6	0·22	44
6·2	0·20	40
6·8	0·16	32
7·2	0·10	20

TABLE IB.

M- Acetate buffer.

The mixture consisted of *M*- acetate buffer (1 c.c.), enzyme solution (2 c.c.) and ascorbic acid solution (1 c.c., 0·5 mg.).

p_H.	Amount of ascorbic acid oxidised.	Percentage of oxidation
4·5	0·20 mg.	40%
5·0	0·31	62
5·6	0·28	56

These experiments indicate that in citrate-phosphate buffer the optimum p_H is 5·6, whereas in *M*- acetate buffer it is about p_H 5·0.

B. Time of Complete Oxidation.

The mixture consisted of ascorbic acid solution (1 c.c.) containing 0·5 mg. of ascorbic acid, enzyme solution (2 c.c.) and M. acetate buffer (1 c.c.) incubated at 40°.

TABLE II.

Time.	Amount of ascorbic acid remaining unoxidised.	Percentage of oxidation.
5 min.	0·25 mg.	50%
10	0·20	60
15	0·12	72
30	0·00	100
45	0·00	100
60	0·00	100

Under these conditions of experiment, therefore, it would seem half an hour's incubation would be sufficient for the complete oxidation of 0·5 mg. of ascorbic acid.

C. Keeping the time and enzyme concentration constant, the relationship between the amount of oxidation and the concentration of the substrate was sought to be obtained.

The mixture consisted of *M*- acetate buffer (1 c. c.), enzyme solution (1 c.c.) and ascorbic acid solution of different concentrations. This was incubated at 40° for 5 minutes.

TABLE III.

Amount of ascorbic acid added.	Amount of ascorbic acid oxidised.
0·5 mg.	0·20 mg.
0·25	0·21
0·20	0·17
0·15	0·13
0·10	0·10

These results show that in the system, which we are using, with the given amount of enzyme maximum oxidation occurs when 0·25 mg. of ascorbic acid is present in 1 c. c. of solution. This information was necessary in connection with certain work on the estimation of ascorbic acid which is in progress in this laboratory (Sen-Gupta and Guha, *J. Indian Chem. Soc.*, 1937, **14**, 95).

D. Specificity.—It was observed that the enzyme preparation was unable to oxidise glutathione, cysteine, hydroquinone and sodium thiosulphate. It must, therefore, be considered fairly specific. It should, however, be stated in this connection that its specificity may not be entirely strict, as recent investigations (Zilva, *Biochem. J.*, 1936, **30**, 1215) indicate that the ascorbic acid oxidase preparation from cucumber can also oxidise in varying degrees substances structurally closely related to ascorbic acid.

E. Inhibitors.—Potassium cyanide in concentration of *M*/1000 completely inhibits the action of the enzyme in a mixture of the type used in sections A and B. Sodium fluoride (*M*/10) seems to have a very slight inhibiting action on the enzyme preparation.

SUMMARY.

A preparation of ascorbic acid oxidase has been obtained from the white gourd (*Benincasacriapra*). Its properties, conditions of activity, specificity and the effect of certain reagents on its action are described.

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SYNTHESIS OF COUMARINS FROM PHENOLS AND ACETOACETIC ESTERS. CONSTITUTION OF HALOGENATED RESORCINS AND ORCINS.

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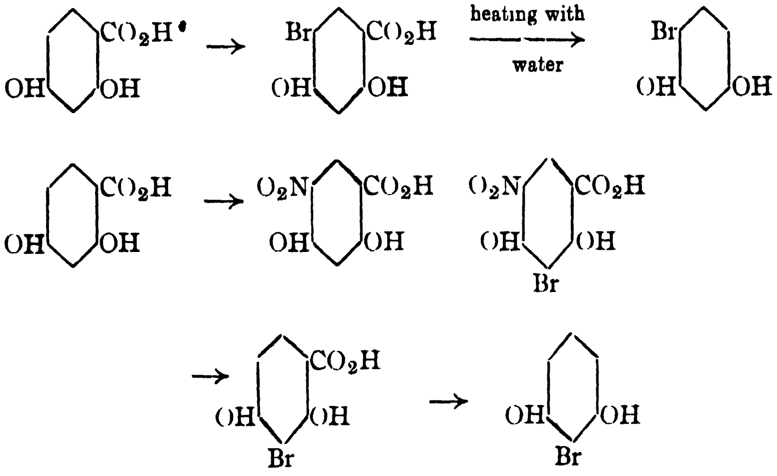
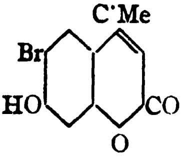
The condensation of halogenated and negatively substituted phenols with β-ketonic esters forming substituted coumarins (Chakravarti and Ghosh, *J. Indian Chem. Soc.*, 1935, **12**, 622) has furnished a ready means for determining the constitution of the substituted phenols. The present investigation was undertaken with a view to determine the constitution of bromoresorcins and the chloro- and bromo-orcins.

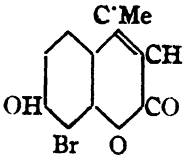
Two bromoresorcins, evidently 4-bromo- and 2-bromoresorcin, are described in literature and they have been prepared in the following way (*cf.* Zehenter, *Monatsh.*, 1887, **8**, 293; Hemmelmayer, *ibid.*, 1914, **35**, 1):



On condensation with acetoacetic ester in presence of sulphuric acid (Pechmann's reaction) these bromoresorcins would form either 7-hydroxy-6-bromo-4-methylcoumarin (I) or 7-hydroxy-8-bromo-4-methylcoumarin (II). These coumarins have, therefore, been synthesised by a method which leaves no doubt about their constitution. 8-Nitro-7-hydroxy-4-methylcoumarin, the nitration product of β-methylumbelliferone (Chakravarti and Ghosh,



(I)



(II)

J. Indian Chem. Soc., 1935, **12**, 791), on reduction with stannous chloride and hydrochloric acid gives 8-amino derivative, which forms a stable diazoanhydride and the latter on treatment with cuprous bromide in hydrobromic acid gives (II). Similarly 6-nitro-β-methylumbelliferone-methyl ether, obtained by the nitration of the methyl ether of β-methylumbelliferone (*cf.* Chakravarti and Banerjee, *J. Indian Chem. Soc.*, 1937, **14**, 37) gives the methyl ether of (I).

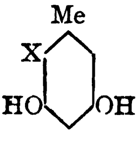
The preparation of bromoresorcins, however, has been attended with practical difficulties. The bromoresorcin of Zehenter (*loc. cit.*) could not be obtained by following the experimental conditions recorded by him and it has been prepared by a modification of the method (*vide* experimental). It readily undergoes Pechmann's condensation with acetoacetic ester and alkyl acetoacetic esters forming coumarins. The coumarin derived from this bromoresorin and acetoacetic ester has been found to give a methyl ether (m.p. 245°), which is identical with the methyl ether of (I) and is, therefore, 6-bromo-7-hydroxy-4-methylcoumarin and the bromoresorcin from which it is derived is, therefore, 4-bromoresorcin. Attempts to prepare the second bromoresorcin by the method described in literature failed. The synthesis of 2-bromoresorcin by other methods was not successful. In attempting to synthesise 2-bromoresorcin by brominating the disulphonic acid of resorcin and then removing the sulphonic groups by steam distillation (*cf.* preparation of 2-nitroresorcin, Kaufmann and Pay, *Ber.*, 1904, **37**, 716) it has been found that excess of bromine produces tribromoresorcinol (m.p. 111°) with the replacement of the sulphonic groups. But if one molecule of bromine is used for the bromination of resorcindisulphonic acid, then after passing superheated steam at 180°, 4-bromoresorcin is obtained instead of 2-bromoresorcin. That the bromoresorcin, thus obtained, is 4-bromoresorcin is proved by the condensation with acetoacetic ester forming (I), (m.p. 278°) identical with the coumarin obtained from bromoresorcin derived from β-resorcylic acid. The troublesome method of preparing 4-bromoresorcin from resorcylic acid may be conveniently replaced by this less cumbrous method and the yield is also satisfactory in this case.

The halogenated orcins, *e.g.* monochloro-orcin and monobromo-orcin have also been prepared and their constitution determined by the formation of substituted coumarins from them.

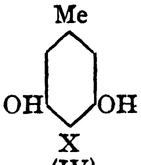
(*a*) *Monochloro-orcin* has been prepared by the action of the calculated quantity of sulphuryl chloride on a dry ethereal solution of orcin. Excess of sulphuryl chloride leads to the formation of polychlorinated derivatives.

(*b*) *Monobromo-orcin* was prepared by Lamparter (*Annalen*, 1865, **134**, 258) by the action of bromine water on orcin but it has now been very conveniently prepared by passing a slow stream of carbon dioxide containing bromine vapour through an aqueous solution of orcin.

These two halogenated orcins readily undergo Pechmann's condensation forming substituted coumarins with acetoacetic ester or its alkyl derivatives. These substituted coumarins may be 5-hydroxy- or 7-hydroxycoumarins according as the chloro-orcin and bromo-orcin have the alternative structures (III) or (IV).



(III)



(IV)

(X=Cl or Br)

The 7-hydroxycoumarins can be easily distinguished from 5-hydroxycoumarins by their fluorescence in alkaline solution. 7-Hydroxycoumarins (umbelliferones) are always fluorescent in alkaline solution and this property is entirely absent in the case of the 5-hydroxy-coumarins. (*cf.* Collie and Chrystall, *J. Chem. Soc.*, 1907, 1804 ; Dey, *ibid.*, 1915, **107**, 1614, 1621 ; Chakravarti, *J. Indian Chem. Soc.*, 1931, **8**, 407 ; Shah and Mehta, *ibid.*, 1936, **13**, 359). The products obtained by condensing chloro- and bromo-orcin with acetoacetic ester and its alkyl derivatives have been found to give only an intense yellow solution in alkali without any flourescence and they are, therefore, 5-hydroxycoumarins.* Chloro-orcin is, therefore, 4-chloro-orcin and bromo-orcin is 4-bromo-orcin. If they were 2-chloro- or 2-bromo-derivatives of orcin (IV) the coumarins derived from them would be 7-hydroxycoumarins exhibiting the characteristic blue fluorescence in alkaline solution.

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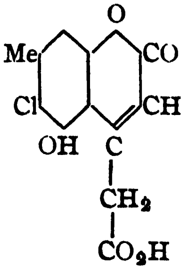
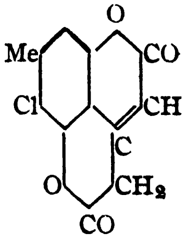
* The coumarins derived from the halogenated orcins may be 6- or 8-halogenated derivatives and they are described in this paper as 6-halogenated coumarins.

The above conclusion has been further confirmed by condensing chloro-orcin with acetone dicarboxylic acid giving rise to a coumarin acetic acid (V), which when heated at 150-60° for several hours yielded a lactone (VI) with the elimination of a molecule of water.



(V)



(VI)

The bromoresorcin and the halogenated orcins have been submitted to Simonis' reaction and as expected since they form coumarins with good yields in the presence of sulphuric acid they also form coumarins and not chromones by changing the condensing agent for phosphorus pentoxide according to Simonis. Thus the generalisation made by Chakravarti (*J. Indian Chem. Soc.*, 1932, **9**, 31) holds true in this case also. In order to study the effects of substituents in the acetoacetic ester molecule on the course of the reaction, bromoresorcin and the halogenated orcins have been condensed with methyl and ethyl acetoacetic esters. These condense most readily with good yields forming coumarins either in the presence of sulphuric acid (Pechmann's reaction) or phosphorus pentoxide (Simonis' reaction).

EXPERIMENTAL.

4-*Bromoresorcin* (*cf.* Zehenter, *loc. cit.*).—It was obtained by boiling monobromoresorcylic acid (1 part) with water (10 parts) acidified with a few drops of dilute sulphuric acid for 16 hours. The solution was then extracted with ether, the ethereal extract washed with dilute ammonium carbonate solution, dried over calcium chloride, the ether removed, when monobromoresorcin was obtained as a solid crystalline mass, m.p. 99·5°.

6-*Bromo*-7-*hydroxy*-4-*methylcoumarin*.—To a mixture of bromoresorcin (4 g.) and acetoacetic ester (3 g.), cooled in ice, concentrated sulphuric acid (*d* 1·84, 10 c.c.) was slowly added with continuous shaking. The solution was kept overnight and poured into ice when a greyish solid separated. It was collected and crystallised from glacial acetic acid (charcoal) as colourless prisms, m.p. 278°. (Found : Br, 31·15. $C_{10}H_7O_3B$ requires Br, 31·36 per cent).

The *acetyl* derivative, prepared as usual by heating with acetic anhydride and sodium acetate, crystallised from dilute alcohol as colourless needles, m.p. 170°. (Found : Br, 26·82. $C_{12}H_9O_4Br$ requires Br, 26·93 per cent).

The identical compound was prepared using phosphorus pentoxide as the condensing agent (m.p. and mixed m.p. 278°; the acetyl derivative, m.p. 170°).

6-Bromo-7-hydroxy-3:4-dimethylcoumarin was obtained from bromoresorcin and methyl acetoacetic ester either in the presence of sulphuric acid or phosphorus pentoxide. It crystallised from glacial acetic acid as colourless silky needles, m.p. 275°. (Found : Br, 29·06. $C_{11}H_9O_3Br$ requires Br, 29·74 per cent).

The *acetyl* derivative crystallised from dilute alcohol in silky needles, m.p. 162°. (Found : Br, 25·53. $C_{13}H_{11}O_4Br$ requires Br, 25·72 per cent).

6-Bromo-7-hydroxy-4-methyl-3-ethylcoumarin from bromoresorcin and ethyl acetoacetic ester (with sulphuric acid or phosphorus pentoxide) crystallised from glacial acetic acid as colourless silky needles, m.p. 240°. (Found : Br, 27·96. $C_{12}H_{11}O_3$ Br requires Br, 28·26 per cent).

The *acetyl* derivative crystallised from dilute alcohol in colourless needles, m.p. 152°. (Found : Br, 24·28. $C_{14}H_{13}O_4$ Br requires Br, 24·62 per cent).

8-Bromo-4-methylumbelliferone.— 8-Diazoanhydride-4-methylumbelliferone (7 g., Pechmann and Obermiller, *Ber.*, 1901, **34**, 666) was dissolved in the least quantity of concentrated hydrobromic acid and the solution added to cuprous bromide solution (prepared by adding 150 c.c. of concentrated hydrobromic acid to 15 g. of copper carbonate and heating with copper turnings till colourless) in the cold. The reddish-brown precipitate was washed with concentrated hydrobromic acid and then with water. It was crystallised as light brown prisms from glacial acetic acid, m.p. 251-52°. (Found : Br, 31·2. $C_{10}H_7O_3$ Br requires Br, 31·37 per cent).

6-Bromo-β-methylumbelliferone Methyl Ether.—The solution of β-methylumbelliferone methyl ether-6-diazobromide, obtained from 6-amino-β-methylumbelliferone methyl ether, was added to cuprous bromide solution in the cold. The brown precipitate obtained was washed with hydrobromic acid and water and crystallised from glacial acetic acid as colourless prisms, m.p. 245°.

The identical compound was obtained by methylating the coumarin obtained by the condensation of bromoresorcin with acetoacetic ester with dimethylsulphate and alkali (m.p. and mixed m.p. 245°). (Found : Br, 29·49. $C_{11}H_9O_3$ Br requires Br, 29·74 per cent).

Preparation of 4-*Bromoresorcin from Resorcin-disulphonic Acid.*—Resorcin (44 g.) was heated on the water-bath with fuming sulphuric acid (15%, 85 c.c.) and concentrated sulphuric acid (*d* 1·84, 85 c.c.) and the precipitated disulphonic acid was collected and washed with glacial acetic acid. It was washed with benzene and the dried substance dissolved in 300 c.c. of glacial acetic acid and bromine (34 g.) added drop by drop. The solution was then diluted with water and distilled with superheated steam at 180° and the residual solution on cooling was filtered and the filtrate extracted with ether The ethereal extract was washed with a dilute solution of ammonium carbonate and water, the ether removed and the oil was left in the desiccator when it solidified. It was crystallised from water, m.p. 99°, yield 15 g. (mixed m.p. with bromoresorcin from resorcylic acid, 99°).

The compound, thus obtained, was proved to be 4-bromoresorcin by its condensation with acetoacetic ester in the presence of sulphuric acid, m.p. 278° and the acetyl derivative melted at 170°.

It has been observed incidentally that if the disulphonic acid of resorcin is brominated with excess of bromine, a voluminous crystalline precipitate immediately separated which crystallised from glacial acetic acid as colourless needles, m.p. 111°. It has been identified to be tribromoresorcin.

Preparation of 4-*Chloro-orcin.*—Sulphuryl chloride (17 g.) was added drop by drop to a cooled solution of orcin (28 g.) in dry ether. At first there was little evolution of sulphur dioxide and hydrogen chloride but after some time the reaction was vigorous. The ethereal solution was washed at first with dilute sodium carbonate solution and then with water. The ether was removed and the product distilled at 138-39°/4 mm., m.p. 104°, yield 9 g. (Found : Cl, 22·68. $C_7H_7O_2Cl$ requires Cl, 22·39 per cent.).

When *anhydrous* orcin (25 g.) was chlorinated with sulphuryl chloride (20 g.) in dry ether as above the product distilled at 140-50°/5 mm. It was redistilled at 142°/5 mm., m.p. 135°, yield 12·5 g. It is probably a polychlorinated orcin.

6-*Chloro*-5-*hydroxy*-4:7-*dimethylcoumarin.*—It was prepared from chloroorcin and acetoacetic ester either in the presence of sulphuric acid or phosphorus pentoxide in the usual manner. It crystallised from glacial acetic acid in colourless prisms, m.p. 264°, yield 4·5 g. (Found : Cl, 15·36. $C_{11}H_9O_3Cl$ requires Cl, 15·81 per cent).

The *acetyl* derivative crystallised from alcohol in needles, m.p. 167°. (Found : Cl, 12·82. $C_{13}H_{11}O_4Cl$ requires Cl, 13·32 per cent).

6-*Chloro*-5-*hydroxy*-3:4:7-*trimethylcoumarin* from chloro-orcin and methyl acetoacetic ester (in the presence of sulphuric acid or phosphorus pentoxide) crystallised from glacial acetic acid, m.p. 276°. (Found : Cl, 14·46. $C_{12}H_{11}O_3Cl$ requires Cl, 14·88 per cent).

The *acetyl* derivative crystallised from alcohol in colourless needles, m.p. 182°. (Found : Cl, 12·72. $C_{14}H_{13}O_4Cl$ requires Cl, 12·65 per cent).

6-*Chloro*-5-*hydroxy*-4:7-*dimethyl*-3-*ethylcoumarin* was obtained by condensing chloro-orcin with ethyl-acetoacetic ester in the presence of sulphuric acid or phosphorus pentoxide. It crystallised from glacial acetic acid, m.p. 210°. (Found : Cl, 14·28. $C_{13}H_{13}O_3Cl$ requires Cl, 14·06 per cent).

The *acetyl* derivative crystallised from dilute alcohol in needles, m.p. 173°. (Found : Cl, 11·68. $C_{15}H_{15}O_4Cl$ requires Cl, 12·05 per cent).

6-*Chloro*-5-*hydroxy*-7-*methyl*-4-*acetic Acid*.—This was prepared from chloroorcin, citric acid and sulphuric acid by the method of Dey and Row (*J. Indian Chem. Soc.*, 1924, **1**, 112). It crystallised from dilute alcohol as needles, m.p. 275°-80°. (Found : Cl, 13·04. $C_{12}H_9O_5Cl$ requires Cl, 13·22 per cent).

The lactone of this acid was obtained by heating the acid at 150°-60° for several hours. It crystallises from dilute alcohol and is insoluble in dilute sodium carbonate solution. (Found : Cl, 14·42. $C_{12}H_7O_4Cl$ requires Cl, 14·17 per cent).

Preparation of Monobromoorcin.—A slow stream of carbon dioxide was passed through bromine (9 g.) and the carbon dioxide carrying the bromine vapour was passed into an aqueous solution of orcin (20 g. in 400 c.c. of water). The solution was filtered and on concentrating the filtrate dark brown crystals separated. It was recrystallised from water, m. p. 142°. (Found : Br, 39·48. Calc. for $C_7H_7O_2Br$: Br, 39·41 per cent).

6-*Bromo*-5-*hydroxy*-4:7-*dimethylcoumarin*, prepared from bromo-orcin and acetoacetic ester as usual either in the presence of sulphuric acid or phosphorus pentoxide, crystallised from glacial acetic acid as prisms, m.p. 217°. (Found : Br, 30·04. $C_{11}H_9O_3Br$ requires Br, 29·74 per cent).

The *acetyl* derivative crystallised from dilute alcohol as needles, m.p. 197°. (Found : Br, 25·13. $C_{13}H_{11}O_4Br$ requires Br, 25·72 per cent).

6-*Bromo*-5-*hydroxy*-3:4:7-*trimethylcoumarin*, from bromo-orcin and methyl acetoacetic ester, crystallised from glacial acetic acid, m.p. 195°. (Found : Br, 27·63. $C_{14}H_{11}O_3Br$ requires Br, 28·26 per cent).

The *acetyl* derivative crystallised from dilute alcohol as needles, m.p. 158-59°. (Found : Br, 24·96. $C_{12}H_{13}O_4Br$ requires Br, 24·62 per cent).

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STUDIES ON SULPHONAMIDES.

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Recently it has been found that 4-aminobenzenesulphonamide possesses a bacteriostatic and bactericidal action against haemolytic streptococci but in clinical application it is necessary to give large doses of the drug by mouth which is sometimes inconvenient and often may give rise to certain toxic symptoms (*cf.* Colebrook and Kenny, *Lancet*, 1936, **I**, 1273; Discombe, *ibid.*, **I**, 626; Goodman and Levy, *J. Amer. Med. Assoc.*, 1937, **109**, 1005; Bucy, *ibid.*, p. 1007). Another drawback is that for its lower solubility in water (2% at the body temperature) it is difficult to administer it in proper doses by injection. It would now be natural to synthesise other compounds more or less chemically related to it and then to study their chemotherapeutic properties.

As the bactericidal property (*cf.* Buttle and co-workers, *Lancet*, 1936, **I**, 1286; 1937, **I**, 1331) is not exclusively due to the presence of the sulphonamide grouping, $-SO_2NH_2$, it was considered to be of interest to replace the amido part by some other group or chain which is known to promote the therapeutic activity in certain other well known drugs. Such groupings were found in 8-aminoquinoline, 6-methoxy-8-aminoquinoline, *p*-anisidine, ethyl *p*-aminobenzoate and δ diethylaminobutylamine, and accordingly, *p*-acetylaminobenzene-sulphonyl chloride prepared according to the method of Schroeter (*Ber.*, 1906, **39**, 1563), was condensed with the above amino compounds in the way described in the experimental part of the paper. The resulting compounds were hydrolysed by dilute hydrochloric acid to afford the different amides of 4-aminobenzene-sulphonic acid.

The examinations of the bacteriostatic activity of 4-aminobenzenesulphon-8′-quinolylamide and 4-aminobenzenesulphon-δ-diethylaminobutyl amide point to the fact that the replacement of the amido hydrgen of *p*-aminobenzenesulphonamide by other chain or group lowers the activity and increases the toxicity of the compound.

EXPERIMENTAL.

4-Aminobenzenesulphon-8′-quinolylamide.—Freshly distilled 8-aminoquinoline (5 g.) was dissolved in dry benzene (25 c.c.) and was slowly treated with *p*-acetylaminobenzene-sulphonyl chloride (8 g.) without allowing the temperature to rise. On stirring the colour of the mixture gradually changed from yellow to orange when it was left overnight. Next day the solid was collected, washed first with benzene and next with ether. This was then triturated with ammonia, filtered and crystallised from alcohol in slender needles, m.p. 192°. (Found : N, 12·45. $C_{17}H_{15}O_3N_3S$ requires N, 12·31 per cent). The above acetyl derivative (4 g.) was heated under reflux for about 1½ hours with 20 c.c. of hydrochloric acid (12%). The solution was cooled in ice and slowly treated with ammonia to make it just alkaline ; the quinolyl amide, which separated out, was filtered and crystallised from alcohol in clusters of needles, m.p., 193°. (Found : N, 14·51. $C_{15}H_{13}O_2N_3S$ requires N, 14·05 per cent).

The substance is almost insoluble in water, but in presence of 2 mols. of hydrogen chloride it forms almost a colourless solution which can be easily sterilised by heating on the water-bath for 1 hour.

4-*Aminobenzenesulphon-6′-methoxy-8′-quinolylamide.* —4-Acetylaminobenzene-sulphonyl chloride (4·8 g.) in a suspension of benzene was mixed with a solution of 6-methoxy-8-aminoquinoline (3·5 g.) in benzene and the resulting mixture was warmed to about 40° on a water-bath for about ½ hour and after 12 hours the solid was collected, dissolved in dilute hydrochloric acid and filtered. The filtrate on neutralisation with ammonia afforded the acetyl derivative of the amide. It separated from alcohol as buff-coloured fine crystals, m.p. 222°. (Found : N, 11·50. $C_{18}H_{17}O_4N_3S$ requires N, 11·32 per cent). The acetyl derivative (3·5 g.) was heated with hydrochloric acid (15 c.c., 6%) for 1 hour under reflux, the solution was filtered hot and the filtrate was carefully neutralised with ammonia when the amide separated out. This was crystallised from rectified spirit in microscopic needles, m. p. 189°. (Found : N, 12·90. $C_{16}H_{15}O_3N_3S$ requires N, 12·76 per cent).

4-*Aminobenzenesulphon-4′-methoxyphenylamide.*—A mixture containing *p*-anisidine (2·6 g.) dissolved in benzene and *p*-acetylaminosulphonyl chloride (5 g.) was left overnight. Next day the solid separating was collected and crystallised from rectified spirit in small prismatic needles, m.p. 197°. (Found : N, 8·93. $C_{15}H_{16}O_4N_2S$ requires N, 8·75 per cent).

On hydrolysing the product with hydrochloric acid and neutralising the resulting solution with ammonia, aminobenzenesulphonanisidide was easily obtained and crystallised from dilute alcohol (4 : 1) in long prismatic needles, m.p. 195°. (Found : N, 10·28. $C_{13}H_{14}O_3N_2S$ requires N, 10·07 per cent).

4-*Aminobezenesulphon-δ-diethylaminobutylamide.*—A solution of δ-diethylaminobutylamine (4 g.) in benzene was treated with the acetylsulphonyl chloride (6·4 g.) as usual. After 24 hours the benzene from the reaction mixture was evaporated off and the residual gummy mass was dissolved in minimum quantity of dilute hydrochloric acid, filtered and the filtrate was kept in *vacuo* over sulphuric acid ; crystals gradually separated out and were collected after a fortnight. These were recrystallised from boiling alcohol in clusters of needles, m.p. 172°, and were found to be the hydrochloride of 4-aminobenzenesulphon-δ-diethylaminobutylamide. (Found : N, 12·84 ; Cl, 10·05. $C_{14}H_{25}O_2N_3S$, HCl requires N, 12·52 ; Cl, 10·58 per cent).

4-Acetylaminobenzenesulphon-4′-carbethoxyphenylamide. — Molecular proportions of 4-acetylaminobenzene-sulphonyl chloride and ethyl *p*-aminobenzoate were mixed together in presence of benzene and left overnight. The benzene was evaporated off and the solid was crystallised from alcohol in clusters of microscopic needles, m.p. 220°. (Found : N, 7·72. $C_{17}H_{18}O_5N_2S$ requires N, 7·74 per cent).

In an attempt to condense 2-chloro-5-amino-7-methoxyacridine with 4-acetylaminobenzene-sulphonyl chloride in the customary way, the initial condensation product, the acetyl sulphonamide melting at 317°, was isolated, but during its crystallisation from alcohol it decomposed to 2-chloro-7-methoxyacridone. Work is still in progress in this direction.

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INFLUENCE OF α-PHENYL GROUP IN THREE CARBON TAUTOMERISM. PART I. TAUTOMERISM OF α-PHENYL-αβ-, βγ-UNSATURATED ACIDS AND ESTERS.

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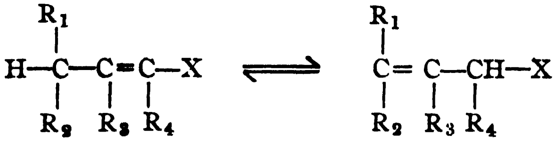
The tautomerism of substances of the general structure



$$H-\overset{\overset{R_1}{|}}{\underset{\underset{R_2}{|}}{C}}-\underset{\underset{R_3}{|}}{C}=\underset{\underset{R_4}{|}}{C}-X \rightleftharpoons \overset{\overset{R_1}{|}}{\underset{\underset{R_2}{|}}{C}}=\underset{\underset{R_3}{|}}{C}-\underset{\underset{R_4}{|}}{CH}-X$$

where R_1, R_2, R_3 and R_4 are alkyl groups or portions of an alicyclic ring and X is a negative activating group like COOH, CO_2Et, COMe and CN has been extensively studied by Kon, Linstead and their collaborators. The influence of methyl and ethyl groups in different positions with respect to the activating groups on mobility and equilibrium of such systems has been investigated (Goldberg and Linstead, *J. Chem. Soc.*, 1928, 2843; Kon and Linstead, *ibid.*, 1929, 1269; Kon and Thakur, *ibid.*, 1930, 2217; Kon, Linstead and Maclenan, *ibid.*, 1932, 2454 etc.) and shown to be in accordance with what was to be expected theoretically from the ionic mechanism first suggested for tautomeric systems by Ingold, Shoppee and Thorpe (*J. Chem. Soc.*, 1926, 1477) and later applied to three carbon systems of the above type in particular by Linstead (*J. Chem. Soc.*, 1929, 2498). Linstead and Williams (*J. Chem. Soc.*, 1926, 2565) studied γ-phenylbutenoic acids and styryl ketones and showed that γ-phenyl group stabilised βγ-phase exclusively which they attributed to the conjugative effect of the phenyl group. In β-phenylhexenoic acids Kon, Linstead and Wright (*J. Chem. Soc.*, 1934, 640) found that the β-phenyl group behaved like a β-methyl group. This was in agreement with the suggestion of Linstead (*loc. cit.*) that the phenyl group in three carbon system behaves as a non-polar group, influencing the mobility and equilibrium of the system by its steric and conjugative effects.

The object of the present work was to study the effect of α-phenyl group in three carbon system terminated by an activating group like COOH and CO_2Et and to compare it with that of α-methyl group already studied by Kon and Thakur (*loc. cit.*) and Kon, Linstead and Maclenan (*loc. cit.*). The methyl group as shown by the above workers depressed the mobility of the the system and shifted the equilibrium to αβ side except in the case of ketones and ethyl α-methyl*cyclo*hexenyl acetate where the βγ-form was favoured. It was, therefore, interesting to see whether this irregular behaviour of the α-methyl group is also shown by the α-phenyl group. In the present work the tautomerism of the following compounds has been studied :

1. α-Phenyl*cyclo*hexylidene acetic acid $\rightleftharpoons$ α-Phenyl*cyclo*hexenylacetic acid.
2. α-Phenyl-Δ^a-hexenoic acid $\rightleftharpoons$ α-Phenyl-Δ^b-hexenoic acid.
3. Ethyl α-phenyl*cyclo*hexylidene acetate $\rightleftharpoons$ Ethyl α-phenyl*cyclo*hexenylacetate.
4. Ethyl α-phenyl-Δ^a-hexenoate $\rightleftharpoons$ Ethyl α-phenyl-Δ^b-hexenoate.

The mobilities and the positions of equilibrium in case of acids were determined under the standard conditions of Linstead (*J. Chem. Soc.*, 1927, 2579). In case of esters the standard conditions of Kon and Linstead (*loc. cit.*) were followed. The iodometric methods of Linstead and May (*loc. cit.*) for the estimation of αβ- and βγ- unsaturated acids and esters in their mixtures were applicable in the present case.

The results are summarised in the following table, the parent acids and esters and the corresponding α-methyl acids and esters being included for comparison.

TABLE I.

Compounds. (only βγ- form shown).	Authors.	αβ-Isomeride at equilibrium.	Mobility $10(K_1+K_2)$.
*cyclo*Hexenylacetic acid	Linstead (*J. Chem. Soc.*, 1927, 355)	12%	1
α-Methyl*cyclo*hexenylacetic acid	Kon and Thakur (*loc. cit.*)	32	0·0075
α-Phenyl*cyclo*hexenylacetic acid	Present authors	42	0·00954
Hexenoic acid	Linstead (*J. Chem. Soc.*, 1928, 2343)	77	7(?)
α-Methyl-Δ^b-hexenoic acid	Linstead (*J. Chem. Soc.*, 1932, 2454). Kon and Maclenan	88	4·882*

TABLE I (contd.).

Compounds.	Authors.	$\alpha\beta$-Isomeride at equilibrium.	Mobility.
α-Phenyl-Δ^b-hexenoic acid	Present authors	87	0·4874
	Esters.		Mobility $(K_1 + K_2) \times 10^4$.
Ethyl *cyclo*hexenyl acetate	Kon, Linstead and Maclenan (*loc. cit.*)	38	8·1
Ethyl α-methyl*cyclo*hexenyl acetate	" "	5	0·15
Ethyl α-phenyl*cyclo*hexenyl acetate		72	0·996
Ethyl hexenoate	Kon, Linstead and Maclenan (*loc. cit.*)	92	153
Ethyl α-methyl-Δ^b-hexenoate	" "	95	151
Ethyl α-phenyl-Δ^b-hexenoate		94·5	35·63

* The mobility of α-methylhexenoic acids as given by Linstead and Maclenan (*J. Chem. Soc.*, 1932, 2454) is 18·8. This seems to be in error. The value for mobility calculated from their experimental results given on page 2455 comes out to be 4·882.

It will be observed that the effect ol α-phenyl group is to depress the mobility in all cases. When compared with the α-methyl group it will be seen that the depression by the α-phenyl group is more than that produced by the α-methyl group in the Δ^a- and Δ^b- hexenoic acids. In the *cyclo*hexane series (acids and esters) the mobility is slightly greater in α-phenyl compounds than in α-methyl compounds.

It will be observed from the above table that the α-phenyl group shifts the equilibrium to the $\alpha\beta$-side in the case of *cyclo*hexene compounds and also in hexenoic acids, but in hexenoic esters there is no such marked effect. When compared with α-methyl compounds it will be seen that the extent of the shift of equilibrium to the $\alpha\beta$-side is much greater in the case of α-phenyl compounds in *cyclo*hexene series. It will be thus seen that the anamoly observed in the case of ethyl α-methyl*cyclo*hexenylacetate in shifting the equilibrium to the $\beta\gamma$-side is non-existent with the α-phenyl group. In the case of hexenoic esters the effect of α-phenyl group and of α-methyl group on equilibrium is of the same order.

The polar effect of the phenyl group is supposed to be of the type + or − T, that is, it is able to furnish either electron accession to or recession from an adjacent carbon atom, according to the sign of the field required at the seat of reaction. + T effect of a phenyl group may be considered negligible in this case since the electronic displacements are opposed to the charge distributing process, and therefore will not be called into play. —T effect of the phenyl group by tending to absorb the charge on the α-carbon atom should increase the mobility and should shift the equilibrium to the αβ-side. The shift of the equilibrium to the αβ-side observed during the course of the present investigation is, therefore, accounted for by —T effect. This view, however, is not in harmony with the depression of mobility.

It seems, therefore, better to regard the effect of α-phenyl group as a nonpolar group as Linstead has suggested (*J. Chem. Soc.*, 1929, 2498). Then the depression of mobility and the shift of equilibrium to the αβ-side will be accounted for by the steric and conjugative effects of the phenyl group.

EXPERIMENTAL.

*α-Phenyl*cyclo*hexylideneacetic Acid*.—α-Phenyl*cyclo*hexenol acetic acid was prepared by a modification of the method of Ivanoff and Spasoff (*Bull. Soc. chim.*, 1932, **49**, 377). The modifications introduced were (*i*) the preparation of sodium salt of phenylacetic acid in aqueous solution instead of in alocholic solution; (*ii*) the use of *iso*propyl bromide in place of *iso*propyl chloride, (*iii*) the use of a mixture of ether and benzene in place of ether; the last two modificattons being necessary due to the high temperature of the laboratory. The yields were the same as those of Ivanoff and Spasoff.

α-Phenyl*cyclo*hexenolacetic acid (10 g.) was gently refluxed on a sand-bath for 3 hours with freshly distilled acetic anhydride (15 c.c). Water was then added and acetic acid removed under reduced pressure. The residue was treated with a solution of sodium bicarbonate and extracted with ether to remove the neutral impurities The sodiim bicarbonate extract was acidified and the precipitated acid was filtered and washed. α-Phenyl*cyclo*hexylideneacetic acid (yield 50%), m.p. 134°, was soluble in benzene, petrol, ether, chloroform and alcohol and best crystallised from dilute alcohol in fine long needles. Its constitution was proved by oxidation to *cyclo*hexanone and benzoic acid. The presence of benzoic acid in the oxidation product is no doubt due to the further oxidation of benzoylformic acid which must have been formed as the first oxidation product. The percentage of iodine absorbed by it under the standard conditions of Linstead and May (*J. Chem. Soc.*, 1927, 2565) is 2·4. The silver and lead salts are insoluble and the barium and calcium salts are somewhat soluble in water. (Found : C, 77·50 ; H, 7·51; Equiv., 216. Ag in the silver salt, 32·57. $C_{14}H_{16}O_2$ requires C, 77·7; H, 7·46; Equiv., 216. $C_{14}H_{15}O_2Ag$ requires Ag, 33·43 per cent). The *anilide* was prepared either (*i*) by the action of aniline on the crude acid chloride and worked up in the usual manner or (*ii*) by heating the acid with aniline for 2 hours at 180°. It crystallised from dilute alcohol, m. p. 146°. (Found : N, 4·9. $C_{20}H_{21}ON$ requires N, 4·81 per cent).

The p-*toluidide* similarly prepared melted at 115°. (Found: N, 4·65. $C_{21}H_{23}ON$ requires N, 4·59 per cent).

*Oxidation of α-Phenyl*cyclo*hexylideneacetic Acid*.—To a solution of the acid (2 g.) in a small quantity of sodium carbonate solution was added potassium permanganate (3·2 g.) dissolved in water (150 c.c.). After the oxidation was complete it was distilled in steam. The presence of *cyclo*hexanone in the distillate was confirmed by the preparation of the semicarbazone, m.p. 168°. The contents of the flask after the steam distillation were filtered and the filtrate concentrated and acidified. The acid thus obtained had m.p. 120° and was identified as benzoic acid by mixed m.p.

*Preparation of α-Phenyl*cyclo*hexenylacetic Acid*.—Ethyl α-phenyl *cyclo*hexenolacetate was prepared by esterifying α-phenyl*cyclo*hexenolacetic acid by Fischer-Speier's method and was crystallised from petroleum ether or dilute methyl alcohol in fine long needles, m.p. 71°. (Found : C, 73·20; H, 8·42. $C_{16}H_{22}O_3$ requires C, 73·29; H, 8·39 per cent).

The results of dehydration of ethyl α-phenyl*cyclo*hexenolacetate by various dehydrating agents are given in the following table, the methods of procedure and working up being exactly the same as described by Kon and Nargund (*loc. cit.*).

TABLE II.

Reagent.	Yield of the unsaturated ester.	J.	$\beta\gamma$.
P_2O_5	70 %	34·6	95·0%
$SOCl_2$	65	32·0	80·0
$POCl_3$	65	25·0	56·0
$KHSO_4$	55	21·2	42·0

The column J in the above table idicates the % of iodine absorbed by the unsaturated ester fraction under the standard conditions of Linstead and May (*loc. cit.*). The last column shows the percentage of $\beta\gamma$- isomeride in the unsaturated ester fraction as found with the help of the reference curve given on p. 744.

The results show that the maximum amount of $\beta\gamma$- unsaturated ester is obtained by the use of phosphorus pentoxide. The unsaturated ester fraction obtained by dehydrating ethyl α-phenyl*cyclo*hexenol acetate by phosphorus pentoxide was hydrolysed in cold and the resulting acid purified by treatment with sodium bicarbonate solution. α-Phenyl*cyclo*hexenylacetic acid is soluble in ether, benzene and alcohol. It is best crystallised from petrol in long colourless needles, m.p. 107°-8°. (Found: C, 76·90; H, 7·22; Equiv., 216·8; Ag in the silver salt, 34·05. $C_{14}H_{16}O_2$ requires C, 77·7; H, 7·46 per cent; Equiv., 216·0. $C_{14}H_{15}O_2Ag$ requires Ag, 33·46 per cent).

The *anilide* was soluble in alcohol, ether, chloroform and benzene and was crystallised from dilute alcohol, m.p. 168°. (Found: N, 4·78. $C_{20}H_{21}ON$ requires N, 4·81 per cent).

The p-*toluidide* melted at 174°. (Found: N, 4·45. $C_{21}H_{23}ON$ requires N, 4·69 per cent).

*Oxidation of α-Phenyl*cyclo*hexenylacetic Acid.*—To a solution of the acid (6 g.) in a small quantity of caustic potash solution was added a solution of potassium permanganate (9·48 g.) in water (300 c.c.). After the oxidation was complete the precipitated manganese dioxide was filtered and the filtrate concentrated and acidified. The product thus obtained after recrystallisation from benzene melted at 98° and was identified as glutaric acid. The filtrate was extracted with ether and the recovered product had m.p. 152° and was identical with phenylmalonic acid.

α-Phenyl-Δ^a-hexenoic Acid.—α-Phenyl-β-hydroxyhexoic acid (10 g.) of Ivanoff and Nicoloff (*Bull. Soc. chim.*, 1932, **51**, 1325) was refluxed with acetic anhydride (15 c.c.) for 3 hours on a sand-bath and worked up in the usual way. α-Phenyl-Δ^a-hexenoic acid (yield 50 %) is soluble in ether, benzene, chloroform, ethyl acetate, alcohol and petrol. It crystallises in long needles when its solution in petrol is cooled in ice, m.p. 70-71°. Silver, calcium, barium and copper salts are insoluble in water. (Found: C, 75·60; H, 7·40; Equiv., 190·3; Ag in silver salt, 36. $C_{12}H_{14}O_2$ requires C, 75·78; H, 7·37 per cent; Equiv., 190·0. $C_{12}H_{13}O_2Ag$ requires Ag, 36·36 per cent).

The *anilide* crystallised from chloroform and petrol, m.p. 130°. (Found. N, 5·2. $C_{18}H_{19}ON$ requires N, 5·28 per cent).

The p-*toluidide* crystallised from a mixture of chloroform and petrol, m.p. 210°. (Found: N, 5·02. $C_{19}H_{20}ON$ requires N, 5·0 per cent).

Oxidation of α-Phenyl-Δ^a-hexenoic Acid.—The acid (3·8 g.), just neutralised with caustic potash, was treated in cold with a solution of potassium permanganate (6·32 g.) in water (300 c.c.). After the oxidation was complete manganese dioxide was filtered off and the filtrate concentrated and acidified. The sticky mass which separated was crystallised from hot water, m.p. 121° and was identified as benzoic acid by mixed m.p. The filtrate was extracted with ether, dried and the substance recovered. A liquid having a characteristic smell was obtained which was identified as butyric acid by its calcium salt.

α-Phenyl-Δ^b-hexenoic Acid.—Ethyl α-phenyl-β-hydroxyhexoate, prepared by the Fischer-Speier's method from the corresponding β-hydroxy-acid of Ivanoff and Nicoloff (*loc. cit.*) was a colourless liquid, b.p 165°/10 mm., $D_{33}°$, 1·0236, and refractive index, 1·49514 at 33°. (Found : C, 71·05 ; H, 8·5. $C_{14}H_{20}O_3$ requires C, 71·18 ; H, 8·47 per cent).

The effect of various dehydrating agents on ethyl α-phenyl-β-hydroxyhexoate is given in the following table, the conditions of experiments and working being the same as in the corresponding *cyclo*hexane compound.

TABLE III.

Reagent.	Yield of the unsaturated ester.	J.	βγ.
P_2O_5	71%	33·0	95%
$SOCl_2$	60	3·7	5·0
$POCl_3$	50	2·6	4·0
$KHSO_4$	50	2·0	2·0

It is evident, therefore, that phosphorus pentoxide is the best reagent for dehydration. The unsaturated ester fraction obtained by the dehydration of ethyl α-phenyl-β-hydroxyhexoate by phosphorus pentoxide was hydrylysed in the cold and the crude unsaturated acid recovered in the usual manner. It was partially esterified and the pure ester obtained was then again hydrolysed in the cold and the acid recovered.

α-Phenyl-Δ^b-hexenoic acid is a liquid, b.p. 155°/10 mm. The acid became a solid crystalline mass when cooled in a freezing mixture and melted at about −15°. The barium and calcium salts are soluble and the silver and copper salts are insoluble. (Found : C, 75·65 ; H, 7·20 ; Equiv., 190·1 ; Ag in the silver salt, 36·01. $C_{12}H_{14}O_2$ requires C, 75·78 ; H, 7·37 per cent; Equiv., 190·0. $C_{12}H_{13}O_2Ag$ requires Ag, 36·6 per cent).

The *anilide* was prepared by the method of Douglas Hardy (*J. Chem. Soc.*, 1936, 391). Aniline (2g.) was slowly added to a cooled solution of ethyl magensium iodide, prepared from magnesium (0·5 g.), ethyl iodide (4 g.) and dry ether (30 c.c.). When the evolution of ethane ceased ethyl α-phenyl-Δ^b-hexenoate (1·5 g.) was added and the solution was warmed on a water-bath for 15 minutes. It was then decomposed with hydrochloric acid and the ether extract was washed with sodium bicarbonate solution. The solid recovered was recrystallised from benzene and petrol, m.p. 100°. It is soluble in alcohol, ether, benzene and chloroform. (Found : N, 5.44. $C_{18}H_{19}ON$ requires N, 5.28 per cent).

Oxidation of α-Phenyl-Δ^b-hexenoic Acid.—The acid (3·8 g.), just neutralised with caustic potash, was treated in the cold with a solution of potassium permanganate (6·32 g. in 300 c.c. of water). When the oxidation was complete, manganese dioxide was filtered off and the filtrate was concen tated and acidified and distilled in steam. The distillate, which was acidic, was extracted with ether. The ether layer was dried and ether removed. The residue was identified as propionic acid by converting it into *p*-nitrobenzyl ester. The contents of the flask after steam distillation were extracted with ether and the ether removed when a solid was obtained, m.p. 152°, mixed m.p. with an authentic specimen of phenylmalonic acid, 151-52°.

Equilibrium and Mobility of the Acids. Conditions of Mobility and Equilibrium. Calculations of Mobility and Methods of Estimation.

Mobility of the acids was determined under the standard conditions of Linstead (*J. Chem. Soc.*, 1927, 2581) *viz.*, heating the acid (1 mol.) with 25% caustic potash (10 equiv.) on a boiling water-bath. These conditions were insufficient for determining the equilibrium in some cases, hence the mixture of the acid and caustic potash (proportion of the acid to caustic potash being the same as above) was boiled in a copper vessel. Experiments for determining the equilibrium were also made, in some cases, starting with mixtures of the acids.

The percentage of αβ- and βγ-form in a mixture of the acids could be determined by the iodometric methods of Linstead and May (*loc. cit.*). The iodine values of the pure acids (J) were first determined and then known mixtures of αβ- and βγ- unsaturated acids were prepared and their iodine value (J) determined experimentally. A curve was then plotted with the iodine value (J) and the percentage compositions of the mixtures as co·ordinate. With the help of this curve, known as reference curve, it was possible to determine the percentage of αβ- and βγ-acids in a mixture recovered from the mobility and equilibration experiments.

Mobility (*M*) was calculated according to the formula,

$$M(K_1+K_2)=\frac{2.3}{T}\log\frac{E}{E-X}$$

where *T* is the time in hours, *E* is the value of *X* at equilibrium and *X* is the change in the time *T*.

The half change period was calculated according to the formula,

$$\text{Half change period} = \frac{1}{K_1+K_2} \log_e 2.$$

The results are summarised in the following tables.

TABLE IV*a*

α-Phenyl*cyclo*hexylideneacetic acid $\rightleftharpoons$ α-Phenyl*cyclo*hexenylacetic acid.

Time = 1 hour. Temperature = 25°.

Reference curve.

% of αβ	... 0	10	30	50	70	90	100
J	... 89·77	82·5	62·92	46·65	37·9	19·81	2·48

Determination of the point of equilibrium.

No. of expt.	Initial material.	Time.	Temp.	J.	αβ as determined from Ref. curve.	Equilibrium.
1	αβ	6 hrs.	B.p.	5	96·5 %	
2	αβ	60	,,	8·54	92·5	
3	βγ	6	,,	87·77	2·5	
4	βγ	33	,,	82·44	10	
5 Mixture	50% αβ	70	,,	54·77	43	
6 Mixture	40% αβ	80	,,	56·87	41	42% αβ
7 Mixture	42% αβ	70	,,	55·8	42	

Determination of the Mobility.

						Mobility 10 (K_1+K_2).
1	αβ	32	100°	3·19	98·5	0·0082
2	αβ	100	,,	7·5	93·5	0·0128
3	βγ	60	,,	88·0	2·5	0·0098
4	βγ	100	,,	87·5	3	0·0078

Average mobility = 10 (K_1+K_2) = 0·00954.
Half change period = 726 hours.
Equilibrium = 42% αβ.

TABLE V.

α-Phenyl-Δ^{α}-hexenoic acid $\rightleftharpoons$ α-Phenyl-Δ^{β}-hexenoic acid.

Time = 1 hour. Temperature = 30°.

Reference curve.

% of αβ	... 0	10	30	50	70	90	100
J	... 34·5	31·44	24·95	18·8	12·7	5·65	2·2

Determination of the Point of Equilibrium and Mobility.

No.	Acid.	Temp.	Time.	J	% of αβ as found from the Ref. curve.	Mobility 10 $(K_1 + K_2)$.	Equilibrium.
1*	αβ	100°	36 hours	5·2	92	0·2651	
2	αβ	„	100	8·5	87		
3*	βγ	„	10	18·4	51	0·881	
4*	βγ	„	36	13·57	67	0·408	
5*	βγ	„	50	11·0	75	0·3957	
6	βγ	„	100	8·5	87		87% αβ

The mobility was calculated from the results marked with*.

Average mobility = 10 $(K_1 + K_2)$ = 0·4874
Half change period = 14·21 hours.
Equilibrium = 87% αβ.

Preparation of Esters.

*Ethyl α-phenyl*cyclo*hexylideneacetate* was prepared from the dry silver salt of the pure α-phenyl*cyclo*hexylideneacetic acid and ethyl iodide in the usual manner, b. p. 175°/12 mm., $D_{33}°$, 1·03651, n^D at 33°, 1·52829 and J, the % of iodine absorbed under the standard conditions of Linstead and May (*loc. cit.*). (Found: $[R_L]_D$, 72·5, Calc. 71·2).

(Found: C, 78·6 ; H, 8·32. $C_{16}H_{20}O_2$ requires C, 78·69 ; H, 8·31 per cent).

*Ethyl α-phenyl*cyclo*hexenyl acetate* was prepared from the dry silver salt of the corresponding pure acid, b. p. 170°/12 mm., $D_{33}°$, 1.0384, n_D at 33°, 1·5177. (Found: $[R_L]_D$, 71, Calc. $[R_L]_D$ 71.2). (Found : C, 78·72 ; H, 8.32. $C_{18}H_{20}O_2$ requires C, 78·69 ; H, 8·31 per cent).

Ethyl α-phenyl-Δ^{α}-hexenoate, prepared from the dry silver salt, had b. p. 145-150°/12 mm., $D_{33}°$, 0.99704 ; n_D at 33°, 1·50209. (Found: $[R_L]_D$

64·53, Calc. $[R_L]_D$, 64.29). (Found : C, 76·95 ; H, 8.4. $C_{14}H_{18}O_2$ requires C, 77·05 ; H, 8·3 per cent).

Ethyl α-Phenyl-Δ^b-hexenoate.—The crude α-phenyl-Δ^b-hexenoic acid was subjected to partial esterification for 2 hours, the following quantities being used : 1 mol. of the acid, 230 c. c. of absolute alcohol and 100 c. c. of 1*N*-alcoholic hydrochloric acid. It was worked up as usual, b. p., 140°/10 mm. D_{33}°, 0·99604, n_D at 33°, 1·49712 ; (Found : $[R_L]_D$, 63·93, Calc. $[R_L]_D$, 64·29). (Found;: C, 76·96 ; H, 8·41. $C_{14}H_{18}O_2$ requires C, 77·05 ; H, 8·3 per cent).

Equilibrium and Mobility of Esters : Conditions of Mobility and Equilibrium and Calculations of Mobility.

The conditions used for mobility and equilibration experiments were those used by Kon and Linstead (*loc. cit.*). The mobility was calculated according to the formula given on page 743 but in this case T is expressed in minutes. Half chage period was also calculated by the formula given on the same page.

Method of Estimation: Linstead and May's iodometric method was used throughout. Reference curve for the iodine value J and composition of mixtures was constructed as usual.

The results of equilibration and mobility experiments are given in the following tables.

TABLE VI.

Ethyl α-phenyl*cyclo*hexylidene acetate $\rightleftharpoons$ Ethyl αphenyl-*cyclo*-hexenyl acetate.

Reference curve.

Time = 1 hour. Temp. = 30°.

% of αβ	... 0	10	30	50	70	90	100
J	... 37·6	32·94	29·2	23·85	18·0	10·44	5·8

Determination of the Position of Equilibrium and Mobility.

No	Iniial ester.	Time	Temp.	J.	% of αβ	Mobility. K_1+K_2
1	α β	24 hours	25°	6·9	99·0	0·0000258.
2	α β	100	,,	12·2	84·0	0·000148.
3	βγ	100	,,	26·87	39·0	0·000130.
4	Mixture 75% αβ	100	,,	17·4	71·0	Equilibrium
5	Mixture 70% αβ	100	,,	16·4	73·0	72% αβ

Average mobility $= (K_1 + K_2) \times 10^4 = 0·996$.
Half change period = 6950.
Equilibrium = 72% αβ

TABLE VII

Ethyl α-phenyl-Δ^{a}-hexenoate $\rightleftharpoons$ Ethyl α-phenyl-Δ^{b}-hexenoate.

Reference curve.

Time = 1 hour. Temp. = 30°.

% of αβ	0	10	30	50	70	90	100
J	34·63	31·6	26·17	19·4	12·2	5·5	1·56.

Determination of the Position of Equilibrium and Mobility.

No	Initial ester.	Time.	Temp.	J.	% of αβ	Mobility. K_1+K_2
1	αβ	5 hours	25°	1·8	99·0	
2	αβ	24	,,	3·1	95·0	
3	βγ	24	,,	3·0	95·0	
4	βγ	10	,,	8·1	82·0	0·003376
5	βγ	5	,,	14·6	64 0	0·00376

Average mobility $(K_1+K_2)\times 10^4 = 35{\cdot}65$
Half change period $= 194{\cdot}2$
Equilibrium $= 95\%\ \alpha\beta$

Our thanks are due to Prof. K. V. Bokil for his interest in this work and to Dr. M. S. Shah for facilities.

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STUDIES IN ADSORPTION OF THE NEUROTOXIN AND HAEMOLYSIN OF COBRA (*NAJA NAJA*) VENOM BY VARIOUS ADSORBENTS AT DIFFERENT P_H, WITH A VIEW TO THEIR ISOLATION.

By S. S. De and B. N. Ghosh.

Dry cobra-venom (*Naja Naja*) has been found to contain as much as 94 % protein. The different toxins and enzymes present in cobra-venom are always found in this protein fraction. In a previous paper (Ghosh and De, *Indian J. Med. Res.*, 1937, **24**, 1175) it has been shown that by cataphoresis of solutions of cobra-venom having different p_H in presence of intercepting membranes of suitable porosity, the neurotoxin and the haemolysin can be freed from more than two-third of the proteins with which they are associated in the crude venom. Since further purification of the toxins by the above procedure did not prove successful, other methods of investigation were tried. Willstätter and co-workers (*Ber.*, 1922, **55**, 3601) obtained satisfactory results in the purification of enzymes by their adsorption on suitable adsorbents and subsequent elution from the surface of these adsorbents. The problem of separation of the neurotoxin and haemolysin of cobra-venom from the admixed proteins, appears to be of a simpler nature to that of the enzymes. The adsorption of neurotoxin and haemolysin of cobra-venom by various adsorbents were therefore studied with a view to ascertain the possibility of their purification by this method.

Adsorption by Silica Gel.

The silica (Merck's) was found to give faintly alkaline reaction in presence of water. It was, therefore, digested with strong hydrochloric acid and then washed with distilled water until free from acid and the p_H of the wash-liquid was about 6·6. A suspension of this silica was prepared containing 208 mg. of SiO_2 per 10 c.c. Ten c.c. of the suspension were mixed with measured volumes of 1% solution of cobra-venom and the total volume made up with a water to 30 c.c. The mixture was then vigorously shaken for 1 hour in a shaker. After this operation the supernatant liquid was separated from the silica by centrifuging and its neurotoxin and haemolysin contents estimated. The neurotoxin was determined by intra muscular injections into pigeons weighing 300-310 g. and the haemolysin was estimated in the way described in a previous paper (*loc. cit.*). The results are recorded in Tables I and II. Assuming that the neurotoxin and haemolysin are adsorbed specifically and independently of each other and that a particle of neurotoxin or haemolysin occupies one active point on the silica surface, an adsorption isotherm can be deduced following the same line of argument as was used in a previous paper (Ghosh, *Indian J. Med. Res.*, 1936, **23**, 285).

The equation is of the form

$$P = \frac{(K_1+C) - \sqrt{(K_1+C)^2 - 4K_0C}}{2} \qquad \ldots \quad (i)$$

where P represents the units of the toxin or lysin adsorbed, K_0 and K_1 are constants and C represents the units of toxin or lysin originally taken. $(C-P)$ gives the number of units of free toxin or lysin as the case may be. The figures given under the heading "Calculated" in Table I and Table II are those calculated from the above equation. It will be noticed that the agreement between the observed and the calculated values is quite good.

TABLE I.

$K_1 = 263$. $K_0 = 222$.

Units of neurotoxin taken C.	Observed. Units of neurotoxin		Calculated. Units of neurotoxin	
	adsorbed.	free.	adsorbed.	free.
120	95	25	90	30
180	125	55	126	54
240	150	90	151	89
300	165	135	169	131
	180	180	181	179
450	200	250	192	258

TABLE II.

$K_1 = 300$. $K_0 = 180$.

Units of haemolysin taken. C.	Observed. Units of haemolysin adsorbed.	Observed. Units of haemolysin free.	Calculated. Units of haemolysin adsorbed.	Calculated. Units of haemolysin free.
120	60	60	61	59
180	78	102	81	99
240	92	148	94	146
300	103	197	110	190
360	115	245	114	246
450	130	320	131	319

Adsorption by Aluminium Hydroxide C.

The aluminium hydroxide C used in these experiments was prepared by Willstätter's method (*Ber.*, 1923, **56**, 149, 1117; 1924 **57**, 1082). A suspension of the gel was prepared such that it contained 228 mg. of Al_2O_3 per 10 c. c. Measured volumes of cobra-venom solution were mixed with 5 c. c. of the suspension of aluminium hydroxide C and the volume made up to 30 c. c. with water. The mixture was shaken for 1 hour and then centrifuged. The supernatant solution was taken and its neurotoxin and haemolysin content estimated. The results are recorded in Tables III and IV.

It will be noticed that the gel adsorbs both neurotoxin and haemolysin fairly strongly. The equation (*i*) is, however, found to be inapplicable in this case. This may be attributed to the fact that their adsorption is not specific as in the case of silica, and the inactive proteins, with which the toxins are mixed, interfere with their adsorption.

TABLE III.

1 C. c. of venom solution contains 100 units of neurotoxin.

Vol. of 1% cobra-venom solution.	Units of neurotoxin taken.	Units of neurotoxin free.	Units of neurotoxin adsorbed.
0·5 c.c.	50	30	20
1	100	66	34
2	200	150	50
4	400	316	84
6	600	500	100
10	1,000	857	143
12	1,200	1,043	157

TABLE IV,

1 C. c. of venom solution contains 30 units of haemolysin.

Vol. of cobra-venom solution.	Units of haemolvsin taken.	Units of haemolysin free.	Units of haemolysin adsorbed.
0·5 c. c.	15	10·0	5·0
1	30	23·0	7·0
1·5	45	36·0	9·0
2	60	50·0	10·0
4	120	104·3	15·7
10	300	272·7	27·3

Comparison of Adsorbing Power of Different Substances.

The adsorbents used in this experiment were silica, aluminium hydroxides C and A, kaolin, kieselguhr and Fuller's earth. The silica was prepared in the same way as described in the previous section. Aluminium hydroxides C and A were prepared according to the prescription of Willstätter and co-workers (*loc. cit.*). The kaoiln, kieselguhr and Fuller's earth (Merck's) were washed with distilled water carefully until free from all electrolytes. Suspensions of these in water were then prepared such that 10 c. c. of the suspension contained 200 mg. of solid in each case. Ten c.c. of the suspension were mixed with 1 c. c. of an 1% solution of cobra-venom and the final volume of the solution was made up to 30 c. c. by the addition of distilled water. It was shaken vigorously for 1 hour in a shaker and then centrifuged. The neurotoxin and the haemolysin contents of the supernatant liquid were determined. The results are recorded in Table V. It will be noticed that for the same weight of the adsorbents, their adsorbing power is in the order : silica > kaolin > aluminium hydroxide C > aluminium hydroxide A > Fuller's earth > kieselguhr.

TABLE V.

	Units adsorbed			Units adsorbed	
Adsorbents.	neurotoxin.	haemolysin.	Adsorbents.	neurotoxin.	haemolysin.
Silica gel	85	64	Alumina A	44	26
Kaolin	75	56	Fuller's earth	30	19
Alumina C	58	38	Kieselguhr	25	15

Stability of the Neurotoxin of Cobra-venom at Different p_H .

It is of importance to know the effect of the reaction of the medium on the stability of neurotoxin of the cobra-venom in connection with the study of its adsorption at different p_H. Since there are no available facts on this point, experiments were carried out to collect the necessary data. In each of a series of small conical flasks were placed 50 mg. of cobra-venom and 5 c.c. of water. The reactions of the solutions of venom were adjusted to the requisite values by adding dilute hydrochloric acid or caustic soda solutions and then to each of them were added 4 c.c. of buffer solutions of the desired p_H. The final volume in each case was made up to 10 c.c. Immediately after the preparation of the solutions their neurotoxin content was ascertained by intramuscular injection into pigeons. After keeping the solutions for 6 hours at room temperature (about 30°) they were placed in a refrigerator at 4° and the neurotoxin content of the solutions was determined from time to time by diluting 1 c.c. of the solution to 40 c.c. with water. The results are recorded in Table VI. It will be noticed that within 24 hours the destruction of neurotoxin in dilute acid is not much, although in dilute alkaline solution it is quite appreciable. The stability of the neurotoxin appears to be maximum between p_H 5·8 and 7·0. It may be stated in this connection that concentrated solutions of dry cobra-venom in distilled water has the p_H 5·8 - 6·0.

TABLE VI.

p_H.	M. L. D. in c.c. of the diluted solution				
	at start.	after 6 hours.	24 hours.	7 × 24 hours.	14 × 24 hours
2·0	0·8	0·8	0·85	1·3	1·6
3·6	0·8	0·8	0·8	1·2	1·45
5·8	0·8	0·8	0·8	0·85	0·9
7·0	0·8	0·8	0·8	0·85	0·9
8·2	0·8	0·8	0·8	0·9	1·1
9·6	0·8	0·8	0·85	1·35	1·7
N/100-NaOH	—	1·0	1·2	3·0	6·9

Effect of Hydrogen ion Concentration on Adsorption.

It has been observed that silica gel adsorbs neurotoxin and haemolysin very strongly. Experiments were, therefore, carried out with this gel at different p_H with a view to determine its effect on the adsorption of neurotoxin and haemolysin. For this purpose 10 c.c. of 0·1% cobra-venom solution were mixed with 8 c.c. of water and adjusted to requisite p_H, 10 c.c. of silica suspension (200 mg.) of the same p_H were then added to it and the volume of the mixture made up to 30 c.c. with distilled water. It was then vigorously shaken for 45 minutes in a shaker. The neurotoxin and haemolysin contents of the supernatant solutions were then determined. The results are recorded in Table VII. It is evident from these data that the adsorptive power of the gel increases with the increase of p_H.

TABLE VII.

p_H.	Units of neurotoxin adsorbed.	Units of haemolysin adsorbed.
4·8	58	15·7
6·0	66	17·3
7·0	70	19·4
8·2	76	20·6
9·4	85	22·4

Purification of Cobra-neurotoxin by Adsorption on and Elution from the Surface of Silica Gel.

From the data recorded in the previous sections it will be noticed that silica gel adsorbs the neurotoxin of cobra-venom very strongly. Since the neurotoxin is a substance of pronounced basic character (Ghosh and De, *loc. cit.*) attempts were made to elute it from silica gel on which it has been previously adsorbed by treatment with solutions of hydrochloric acid of different concentrations. Use of *N*/2-HCl was found to give fairly good results. With less dilute acid the amount of neurotoxin eluted was smaller, while with more concentrated acid the destruction of the the toxins became considerable even during the period of the experiment. The procedure adopted is as follows :— 200 mg. of silica gel, on which the neurotoxin was previously adsorbed in the manner described already, was shaken with 10 c.c. of *N*/2-HCl in a shaker for 30 minutes. The mixture was then centrifuged and the neurotoxin and nitrogen contents of the supernatant solution were determined. The results are recorded in Table VIII. The units of neurotoxin per mg. of N_2 of dry cobra-venom is found to be 16·6. It will be noticed from the data recorded in Table VIII that after elution from silica surface the solution contains 25·3 units of neurotoxin per mg. of nitrogen. Therefore purification attained is only 1·5 times. In the case of haemolysin no purification could be effected, on the contrary, it has become contaminated with more protein.

TABLE VIII.

Units of neurotoxin taken.	Units of neurotoxin eluted.	Total N_2.	Neurotoxin per mg. of N_2.	Units per 1 mg. of N_2 (purified venom). / Units per 1 mg. of N_2 (crude venom).
120	48	1·88 mg.	25·5 units	1·5
240	55	2·32	23·7	1·4
360	60	2·50	24·0	1·4

TABLE IX.

Units of haemolysin taken.	Units of haemolysin eluted.	Total N_2.	Haemolysin per mg. of N_2.	Units per 1 mg of N_2 (purified venom). / Units per 1 mg. of N_2 (crude venom).
120	20	1·88 mg.	10·6 units	0·6
240	28	2·32	12·1	0·7
360	33	2·5	13·2	0·8

This method alone, therefore, does not lead to encouraging results. In the subsequent experiments, a combination of this with other methods were tried. Part of the inactive proteins were first removed by precipitation by treatment with Na_2SO_4, the concentration of the salt in the final mixture being 22%. The mixture, after one hour was centrifuged and the supernatant solution containing the greater part of the neurotoxin was shaken with silica gel at different p_H. The silica was then separated by centrifuging and shaken with 15 c. c. of N/2-HCl for 30 minutes. The results are recorded in Table X. It will be noticed that the maximum purification is effected when the neurotoxin is adsorbed on the silica gel between p_H 3·6 and p_H 5·0 and for the same nitrogen content it amounts to 4·7 times that of the crude dry venom.

TABLE X.

p_H at which neurotoxin is adsorbed.	Neurotoxin eluted.	Amount of N_2 in the elute.	Purification attained.
3·6	29 units	0·373 mg.	4·7 times
5·0	40	0·51	4·7
6·0	52	0·672	4·6
7·4	57	0·86	4·0
9·6	72	1·11	3·9

SUMMARY.

1. The adsorption of neurotoxin and haemolysin of cobra (*Naja Naja*) by a number of adsorbents has been determined. The adsorbing power of the different substances has been found to be in the following order :

Silica > Kaolin > Alumina C > Alumina A > Fuller's earth > Kieselguhr.

2. In the case of silica, the adsorption of neurotoxin and haemolysin has been found to increase with increasing p_H of the silica suspension.

3. The stability of the neurotoxin has been determined at different p_H . It has been found to be maximum between p_H 5·8 and p_H 7·0.

4. By combining the process of adsorption and elution with fractional precipitation of non-toxic proteins by sodium sulphate, it has been possible to concentrate the neurotoxin in a protein fraction which is 21·3% of the protein present in the crude venom.

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REVIEWS

Erzeugung von Eisen und Stahl.—VON PROF. DR.-ING. ROBERT DÜRRER, VORSTAND DES EISENHÜTTENMANNISCHEN INSTITUTS DER TECHNISCHEN HOCHSCHULE, BERLIN. (TECHNISCHE FORTSCHRITTSBERICHTE BAND 39) VIII, 159, PP. WITH 78 FIGURES. DRESDEN 1936; THEODOR STEINKOPFF. R. M. 10-, BOUND R. M. 11. - .

This book constitutes one of the series of the Reports on the Progress of Chemical Technology edited by Prof. Dr. B. Rassow of Leipzig. The purpose of this monograph is to present a brief survey of the latest developments in the production of iron and steel. As the book is intended mainly for the technical chemists, emphasis is laid more on the metallurgical than on the constructional aspect of the treatment ; this, however, does not extend so far into details as are to be found in a book meant for workers in an iron factory.

After a discussion on the general metallurgy of the production of pig iron, dealing with the various systems composed of iron, oxygen, carbon and hydrogen, descriptions of the blast-furnace and the electric furnace processes for pig iron have been given.

In the case of steel, various processes for the production of weld and ingot steel have been described. A discussion of the metallurgical reactions, involved in various systems composed of iron, oxygen, carbon, silicon, manganese, phosphorus and sulphur in the production of ingot steel, is a noteworthy feature of the book. An account of the production of steel in electric furnaces has been given in the final chapter.

The literature references at the end of each section, though not quite complete, is still fairly abundant for all practical purposes.

The book can be recommended to students of metallurgy and technical chemistry, as well as to those actually engaged in research work in this field.

P. R.

Laboratory Manual of Organic Chemistry—BY B. B. DEY AND M. V. S. RAMAN. PUBLISHED BY G. SRINIVASACHARI AND SONS, MOUNT ROAD, MADRAS. PP. X +234+158 +XLV.

The book is divided into two parts, part I is intended to fulfil the requirements of the elementary students, while part II should be suitable for the advanced students. In part I the authors have fully dealt with the practical details of simple operations in organic chemistry, *e.g.*, crystallisation, steam and vacuum distillation, extraction with solvents, etc. and have also given an outline of the technique used in the manipulation of small quantities of substances. The description of all these processes bears eloquent testimony to the experience of the authors in giving practical training to the students.

The identification of organic compounds is often a bugbear to the general students and all teachers of organic chemistry would agree with the authors that " The tendency of students to submit scrappy records of organic analysis is a common enough experience and is to be attributed mainly to the students' idea that the spotting of the substance being his main if not the only problem, the method of experimentation and observa tions leading to the typification and final identification of a substance might usually be given a secondary place." In order to dissuade the students from this wrong idea, the authors have given in an admirable way the methods to be followed in the identification of commoner organic compounds and the systematic scheme thus drawn up is sure to lead to the identification of even complex organic compounds. The authors have also detailed the methods for the preparation of simpler derivatives of these compounds always illustrating by typical examples. Finally ' a few model analyses have been given with a view to help the student in picking up the procedure of recording observations systematically and intelligently and drawing conclusions logically'.

As regards the preparation of organic compounds it is noticed that the preparations, which have been selected most judiciously, illustrate the main reactions in organic chemistry and the second part also contains organic preparations of an advanced character illustrative of special reactions requiring manipulative skill and experimental technique.

The methods for the quantitative estimations of the elements and also of typical groups in organic compounds have also been enumerated with as much practical detail as possible within the small compass of the volume. To add to the usefulness of the book various appendices containing the physical and chemical constants of substances and a complete Index have also been added. It would, however, have been more advantageous if the index to the two parts were not given separately and the numbering of the pages in the two parts were made continuous.

Although there are valuable and separate treatises on organic preparations, on the estimation of the elements and groups in organic compounds and on the identification of organic compounds, this volume is exceptional inasmuch as it contains in itself the preparation, the estimation and the identification of organic compounds and records the minutest practical details so lucidly that students possessing this book may carry on organic practical work without the guidance of a teacher. The authors should be congratulated for supplying to the students and teachers a valuable and useful treatise of this type.

The get up and printing of the book leave nothing to be desired.

D. C.

Journal of the Indian Chemical Society
Vol. XIV, 1937.

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24	Fig. 5	NaOH	KOH
29	Table VI column 4	representing values of *a*	
,,	,,	,, from Eqn. (*ii*) ,,	,, from Eqn "
30	11	Sneolzyk	Smolezyk
32	16-18	,, The variations of the value of *Z* indicate that a true thermodynamic equilibrium between the different phases has not been established under these conditions "	" That the variations ....conditions "
162	2	Equations (*iii*) and (*ii*)	Equations (*iii*) and (*i*)
165	5*	Bartell and Fu	Bartell and Bartell
,,	,,	*Read* (*loc. cit.*) for the reference given	
166	12	,, *J.A.C.S.,* 1934, **56**, 2205	(*loc. cit.*)
243	6	,, It dyes wool in red shades from acid bath and cotton in light red shades from an alkaline hydrosulphite bath	It dyes wool......hydrosulphite vat
,,	1*	5 : 7-dinitroisatin	6 : 7-dinitroisatin
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* From bottom.